ASSESSMENT OF METHODS OF DRY WAY CHLORINATION OF SULPHIDE ORES

for

CANMET, Mineral Sciences Laboratories
Department of Energy, Mines and Resources

February 25, 1986

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CONTRACT SERIAL NUMBER OSQ84-00442
CONTRACTOR Ian J. Reimers
REQUISITION NUMBER 23440-4-9177

ASSESSMENT

of

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of

SULPHIDE ORES

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CANMET MINERAL SCIENCES LABORATORIES

DEPARTMENT OF ENERGY, MINES AND RESOURCES

Ottawa, Ontario

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February 25, 1986

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Assessment of Methods of Dry Way Chlorination
of Sulphide Ores
Contract No. OSQ84-00442

Dear Mr. Ritcey

In accordance with the above contract, we are pleased to submit ten copies of our report on the above project, commissioned by your Department in April, 1985.

Yours very truly,

REGISTERED PROFESSIONAL ENGINEER W. R. N. SNELGROVE PROVINCE OF ONTARIO

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(transmittal letter only)

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ABSTRACT

The technical, economic and environmental aspects of three non-aqueous (dry way) chlorination processes for treating complex sulphide ore concentrates are assessed.

The processes are:

low temperature (∿100°C)
medium temperature (∿300°C)
high temperature (∿600-700°C)

The evaluations are mainly based on test results achieved by CANMET and others on concentrates from complex New Brunswick ores, and opinions are given as to the probability of each of the processes being acceptable to industry in the medium to long term (10-25 years).

INTRODUCTION

SCOPE

On April 12, 1986 CANMET Mineral Services Laboratories of Energy, Mines and Resources awarded Contract No. OSQ84-00442 to Jan H. Reimers and Associates Inc. of Oakville.

Objective

To technically assess three chlorination process options for treatment of sulphide ores, as developed at CANMET. The assessment to include not only technical but also economic and environmental considerations and possible by-product recovery.

Period

April 12, 1986 to November 12, 1985, later extended into 1986, due to deferral of draft report review meeting.

Statement of Work

1. The contractor to develop a good understanding of the three dry way chlorination approaches: low (100°C), medium (300°C) and medium-high temperature (600°C) and establish agreed flowsheets.
2. The contractor to assess the pros and cons of each of the proposed approaches and provide opinions as to the probability of any of these approaches being economically and technically acceptable to industry in the medium to long term (10-25 years).
3. The contractor to also assess the pros and cons of applying the three approaches to the treatment of nickel/copper sulphide ores, including pyrrhotite as an alternative to current SO_2 producing smelter technology.

SOURCE DOCUMENTS

CANMET supplied reports, memos and other relevant documents concerning the test work carried out in their laboratory and by outside contractors.

In addition, Jan H. Reimers and Associates drew on their own in-house

information as required.

MEETINGS

A meeting was held between Mr. G.M. Ritcey of CANMET and J. H. Reimers, J. C. Taylor and W. R. Snelgrove of Jan H. Reimers and Associates, in Oakville on April 30, 1985 to discuss the project.

A further meeting was held at CANMET in Ottawa on June 20, 1985. This meeting, chaired by Mr. Ritcey, was attended by J. H. Reimers, W. R. Snelgrove and a number of CANMET personnel who had been involved in the test work. The processes were discussed, flowsheets were agreed and the medium temperature process was eliminated from further in-depth study.

The draft report was submitted to CANMET on September 25, 1985. Comments from the CANMET staff assigned to this research program, were received with Mr. G. M. Ritcey's letter of November 6, 1985.

The draft report was reviewed at a meeting between Mr. G. M. Ritcey and Mr. W. J. S. Craigen of CANMET, and Mr. J. H. Reimers and Mr. W. R. Snelgrove of Jan H. Reimers and Associates, in Oakville on February 3, 1986.

EXECUTIVE SUMMARY

1. CANMET promoted dry way chlorination because it was considered the only type of complex sulphide treatment process with the potential of converting the iron to a disposable hematite, and at a lower energy cost than for conventional pyrometallurgical and proposed hydrometallurgical processes. Dry way chlorination of sulphides and dechlorination of the resulting iron chlorides with oxygen are both exothermic reactions. Ideally, these main process steps would thus be autogenous, with only the necessary oxygen requiring external energy.

2. For a number of years CANMET has directly, and through work subcontracted to other research institutions, investigated the possibility of treating sulphide ore concentrates by dry way chlorination. This research work has been aimed at the following main objectives:

   2.1 Treat complex zinc-lead-copper-iron sulphide ores or concentrates which cannot be economically processed by methods commercially used at present.

   2.2 Improve the recoveries of base and precious metals, such as copper, lead, zinc, gold and silver, from complex sulphides.

   2.3 Avoid the SO_2 emissions, or the processing of SO_2 smelter or roaster gases to sulphuric acid, connected with conventional treatment of sulphide ores.

   2.4 Also minimize the amounts of pyrite and other sulphides left in tailings or residues discharged to the environment.

   2.5 Instead, recover the ore's sulphur content in the form of elemental sulphur, which can be marketed or safely stockpiled for future use, and the iron in an oxidic form suitable for safe disposal or marketing.

CANMET has also considered the possible application of this approach to nickel-copper sulphide ores, as the smelting of these is at present the most important metallurgical source of SO_2 emissions in Canada.

3. The three chlorination process alternatives:

   low temperature (~100°C)
   medium temperature (~300°C)
   high temperature (600-700°C)

   have been assessed on the basis of documentation provided by CANMET and available from other sources of information.

   The evaluation is mainly based on results achieved by CANMET and others on zinc-lead-copper-iron sulphide concentrates from complex New Brunswick ores.

4. Common for all three chlorination processes is that iron, usually present at high levels in concentrates from complex sulphide ores, is extensively chlorinated. This reduces the amount of sulphides discharged in the subsequent leach residue, in particular pyrite which remains unreacted in most proposed hydrometallurgical processes. The chlorinated iron must however be removed from the process in an environmentally acceptable form. Also, chlorine combined with this iron must be removed and recycled to the process.

   Proposed iron removal and related chlorine recovery methods are chemically feasible and energy efficient in theory. Practical problems are indicated, however, when projecting these steps to commercial scale. While eliminating the SO_2 emission problem, dry chlorination is likely to create other disposal problems which could be difficult to solve efficiently and economically.

5. The low temperature process presents some problems which would be difficult to solve in a practical way. These include:

   5.1 Separation of the solid reaction product from liquid sulphur chloride (S_2Cl_2) with high sulphur content.

   5.2 Recovery of elemental sulphur from this solution and total recycle of the sulphur chloride, which cannot be discharged to atmosphere.

   5.3 Low reactivity of zinc sulphide with S_2Cl_2.

5.4 Most of the iron is chlorinated and must be removed from the subsequent hydrometallurgical flowsheet as a precipitated iron compound such as ferric hydroxide, likely to be environmentally undesirable and unmarketable in large quantities.

The main advantage of this alternative is that known materials of construction should stand up well to process conditions prevailing at this low temperature.

6. The medium temperature process does not seem to be a practical process. The main reasons are:

6.1 Elemental sulphur cannot be separated from the reaction mass at ~300°C and will accumulate in the system, without any practical outlet for it.

6.2 The sticky, pasty reaction mass cannot be handled in any known type of equipment.

6.3 Ferrous chloride oxidation must be carried out at a considerably higher temperature (at least 450°C); heating such a reaction mass could be very difficult in practice.

7. The high temperature process seems to be technically the most feasible alternative. It avoids to a considerable extent, but probably not entirely, problems connected with sulphur chloride. This is therefore the process we have investigated the most thoroughly, and the only one for which sufficient data were made available to calculate a tentative materials balance.

The main problems connected with this process are listed below.

7.1 Zinc and some other metal chlorides are volatile at the chlorination temperature and must be fully removed to recover byproduct sulphur. This is likely to be difficult in practice.

7.2 The deferrination step (removal of iron as volatile ferric chloride) to produce a chloride melt with low residual iron content, is likely to be a difficult continuous industrial operation.

7.3 A lesser gas stream may have to contain sulphur chloride and could therefore be difficult to recycle.

7.4 The dechlorination process (conversion of $FeCl_3$ to Fe_2O_3 with chlorine recovery) has been tested and is technically feasible. The problem is to produce a granular iron oxide with low heavy metal chlorides content for safe disposal or large scale marketing.

7.5 Although the main reactions are exothermic, heat deficiency must be expected in some auxiliary steps. Auxiliary heat supply could be very difficult in this environment.

7.6 Freezing of splashed and volatilized chlorides could complicate reactor gas cleaning in a fully enclosed system.

Thus, a number of areas would require further research and pilot plant test work, to determine whether high temperature chlorination could be developed into a technically feasible process.

8. The chlorination products from all three processes would be processed by hydrometallurgical flowsheets to recover copper, zinc, lead and silver, as well as chlorine for recycle by electrowinning from chloride solutions. Suitable hydrometallurgical flowsheets would be combinations of individual steps known from other well investigated processes. The hydrometallurgy seems therefore quite feasible, though considerable research and pilot plant operation would be required for adaptation to the chloride products obtained from the different dry chlorination processes, and from a wide range of concentrate compositions.

9. The dry way chlorination processes involve handling and recirculation of environmentally objectionable or poisonous gases, such as chlorine, sulphur vapour, sulphur chloride and metal chloride fumes. Very tight gas systems would therefore be required, with continuous monitoring of possible leaks. Very tight, closely controlled systems involving poisonous gases are widely used in the chemical industry and in some metallurgical processes, of which Inco's carbonyl nickel refining process is a good example. Such requirements do however increase capital, operating and maintenance costs of a plant and

therefore constitutes an important economic factor in the evaluation of dry way chlorination.

10. Industrial application of dry way chlorination processes will almost certainly require introduction of some air or preferably nitrogen into the gas system, for example with the dried concentrates. There, nitrogen will accumulate through recycling and will have to be purged from the gas system to keep it in balance. After removing as much as possible of the chlorine, sulphur, sulphur chloride, etc. by condensation, it will still be necessary to remove residual amounts of these contaminants by wet scrubbing before the nitrogen can safely be expelled to atmosphere.

11. Iron, including pyritic iron, reacts extensively in dry way chlorination.

    11.1 In the low temperature process, iron remains in the chlorides to leaching, and must therefore be removed from the subsequent wet flowsheet. Here, iron disposal problems are therefore similar to those encountered in other hydrometallurgical processes for complex sulphides, but accentuated by additional iron from the concentrate's pyrite content.

    11.2 In the high temperature process, iron is removed as ferric oxide (hematite) by dechlorination of ferric chloride vapour in the gas phase. Available information indicates that this ferric oxide will be extremely fine, possibly still contain some ferric chloride, and therefore not suitable for safe waste disposal or large scale marketing. It could also contain zinc chloride, unless steps are taken to remove it beforehand. It seems possible to obtain a granular ferric oxide, with lower chloride content, but this requires a more complicated and less energy efficient ferric chloride dechlorination method.

12. CANMET is interested in the possible application of dry chlorination to nickel-copper bulk concentrates containing cobalt, platinum group metals and pyrrhotite. The objective would be to recover all the base and precious metals from chloride solution, sulphur in elemental form, and iron as a

hydroxide or similar precipitated residue.

The very limited experimental data available indicate that chlorination, including with S_2Cl_2 at low temperature, would solubilize nickel and copper from Canadian nickel-copper sulphide concentrates. Nevertheless, this approach does not seem a viable alternative to conventional smelting and refining. The main reasons are listed below.

12.1 To achieve an economic nickel mill recovery, considerable amounts of iron must usually be allowed into the nickel concentrate; this applies in particular to Sudbury ores, from which the nickel concentrates contain considerably more iron than nickel. Most of this iron is likely to be chlorinated and must subsequently be removed as iron chloride, oxide or hydroxide. Either way, it creates environmental problems whereas conventional smelting removes iron as inert slag. Iron would also require a large amount of chlorine to be recycled, relative to the nickel, copper, etc. produced.

12.2 Large amounts of iron and copper would have to be separated from a nickel chloride solution.

12.3 Information is lacking on the behaviour of precious metals, in particular that of platinum metals. Their recovery is likely to be more complicated than from conventional smelting and refining.

Chlorination of nickel-copper concentrates could cause serious environmental problems, depending on the nature of the iron compound which would be produced in large quantities. Investment and maintenance costs might be high.

Nickel is extensively extracted from matte by aqueous chlorination as used commercially in some nickel refining processes. Direct chlorination of nickel sulphide concentrate in aqueous suspension would be a simpler alternative. Although doing away with the dry way chlorination problems, this option still seems unattractive for a number of reasons, such as iron removal costs and uncertainties about precious metals recovery.

13. We believe however that for most concentrates, the objectives of:
    - recovering base metals and silver from a chloride solution,
    - recovery of elemental sulphur,
    - removing iron as a residue

    can be achieved, in a simpler fashion and at lower cost, by hydrometallurgical processes based on direct leaching of complex sulphide concentrates in chloride systems, and which have been extensively investigated on pilot plant scale.

14. However, pyrite remains unreacted and gold is not recovered by wet chlorination. High temperature dry chlorination therefore offers the potential of recovering all constituents, including sulphur and iron, from complex sulphides with significant gold and pyrite values. In principle, the process could be applied to ores where precious metal values are locked in with pyrites.

15. Justification for further development of dry chlorination depends on the long term (10-25 years) future outlook for:

    15.1 Sulphur demand, supply and hence price. While sulphur demand is likely to increase, one must also consider that new sulphur sources will come into being from the treatment of environmentally objectionable wastes, such as thermal power station combustion gases, coal treatment, maybe recovery from accumulated sulphide tailings or fertilizer plant gypsum by processing to sulphuric acid, etc.

    15.2 Permissibility of rejecting pyrites in tailings. Pyrite is the least reactive sulphide mineral and is still widely regarded as safe to discard and stockpile. If pyrite disposal becomes unacceptable, then dry chlorination could solve this problem, provided that the pyritic iron can be discarded in a more acceptable form, or turned into a raw material for the steel industry - the only industry capable of consuming large tonnages of iron raw materials. We are not convinced that dry chlorination will provide an answer to this question.

16. The low and high temperature dry way chlorination processes present technical problems which at best would require great efforts and expenditures to solve. Even so, we are not convinced that either would result in a process suitable for practical operation on a commercial scale. Of these, some of the problems connected with the low temperature process seem to us the most difficult to solve, although the high temperature process certainly also presents some very difficult problems. The medium temperature process has been rejected as unpractical.

17. The low temperature process offers a narrow potential application range as it puts practically all the iron into solution and therefore seems unattractive for ores and concentrates with high pyrite and/or pyrrhotite contents. The high temperature process does not have this limitation, provided of course that an acceptable iron oxide product can be obtained from dechlorination. It seems therefore to have a wider potential application range.

18. If the policy making authorities believe that some of the following criteria are valid for the long term (10-25 years) future:

    18.1 processing of very complex ores, even at higher cost, will become necessary to satisfy world metal consumption;

    18.2 conventional smelting will no longer be permitted even when fixing a large proportion of sulphur in the smelter gases (there will always be some SO_2 emission from conventional smelting);

    18.3 pyrite disposal will no longer be tolerated in tailings;

    18.4 an increasing worldwide shortage of sulphur will develop, resulting in high sulphur prices;

    18.5 a large scale use for byproduct ferric oxide can be developed - maybe for new steel processes based on fine raw material feed;

    then further research into dry way chlorination might be justified. It should however be clearly understood that any such development program will be of long duration and require large efforts in personnel as well

as great expenditures, with no assurance that the research will result in practical processes suitable for large scale operations.

Problems with the low and high temperature processes are of different nature and therefore not easily compared. At this point, we are inclined to favour the high temperature process in the event that CANMET decides to do further test work.

19. If one believes that pyrite rejection will continue to be permissible in the long term future, then direct leaching of complex sulphides with ferric or cupric chloride would be a simpler and probably more economic alternative to conventional SO_2 emitting processes. Chloride leaching of sulphides still recovers the non-pyritic sulphur. These processes have been extensively pilot plant tested and we understand that CANMET has embarked on a research program into the ferric chloride leach process.

LOW TEMPERATURE CHLORINATION PROCESS (~100°C)

CONCLUSIONS

The main advantage of low temperature chlorination with S_2Cl_2 is that known materials of construction should stand up well.

On the other hand, the practical application range of this process seems limited to a rather narrow range of complex sulphide materials, due to low reactivity of zinc sulphide and because reacted iron must subsequently be removed from the hydrometallurgical circuit. The chemical and physical characteristics of sulphur and sulphur chloride give us reason to believe that operational problems are likely to occur, which might be difficult to solve under practical plant conditions.

Some of the main problems we see are outlined below.

Zinc Recovery

The main disadvantage is low zinc solubility, i.e. low conversion of ZnS to $ZnCl_2$. This is important since zinc is a major base metal in the largest known complex sulphide ore deposits in Canada (and also in Australia, for example). Unreacted zinc sulphide can be solubilized by leaching with $FeCl_3$ solution, applying known technology. Direct application of ferric chloride leaching to the complex concentrate seems however more logical and much cheaper than going through a prior S_2Cl_2 treatment, particularly as the hydrometallurgical process following leaching would be very similar for both cases.

Pyrite Dissolution

S_2Cl_2 reacts with pyrite which is normally a major constituent of complex concentrates not suitable for conventional processing. Removal of additional iron and sulphur is likely to increase the processing cost much beyond the value of the additional sulphur, while the iron will just increase waste disposal costs.

In contrast, pilot plant tested hydrometallurgical chloride processes (Elkem, Minemet, the CANMET ferric chloride process, etc.) leave unreacted pyrite in leach residue, thereby reducing the amounts of iron and sulphur to be removed from the process itself.

S_2Cl_2-S System

As to the low temperature chlorination process itself, the main

problems derive from the following characteristics of the S_2Cl_2-S system in the 0-130°C temperature range.

1. High solubility of elemental S in S_2Cl_2, and the tendency to form supersaturated solutions. S_2Cl_2 with high S level must therefore be recirculated through the chlorination, even if only a minor side stream is directed through the sulphur crystallization circuit. It also means that the side stream must be cooled to a low temperature in order to achieve a sufficient S solubility differential.

2. High viscosity of S_2Cl_2, which increases rapidly with content of dissolved S.

3. High reactivity of S_2Cl_2 with water, resulting in formation of SO_2, HCl, H_2S and S°, all highly undesirable within and outside the system.

4. Toxic S_2Cl_2 fumes cannot be emitted to atmosphere or workplace. Efficient sealing of all process equipment is therefore necessary.

5. S_2Cl_2 apparently does not react significantly with air at this temperature range, but air must nevertheless be kept out of the system to avoid oxidation and sulphation reactions within it.

The main practical problems created by these characteristics of sulphur monochloride are commented upon below.

Chlorination

The concentrate must be completely dried and the dry concentrate probably purged with nitrogen, before feeding to the chlorination step. This is primarily an economic problem.

The high S level in S_2Cl_2 solution recirculated through the chlorination could adversely affect the chlorination process. According to the Russian paper[6] the reactivity of S_2Cl_2 is sharply reduced on saturation with sulphur. This effect may not have been so evident in batch tests carried out with excess pure S_2Cl_2.

Liquid/Solids Separation

Again, high viscosity could interfere with efficient L/S separation in a pressure filter.

Sulphur Crystallization

Due to supersaturation of sulphur solutions in S_2Cl_2 on cooling, it seems necessary to cool the sulphur recovery side stream to a low temperature (10-30°C) in order to effectively crystallize sulphur while keeping sulphur at a level in the chlorination step (say 35-60% S) where the viscosity might still be manageable and where reactivity does not suffer too much.

High viscosity in combination with a narrow specific gravity differential between S_2Cl_2 solution and S crystals, could make L/S separation difficult even in a centrifuge.

Removal and Recovery of S_2Cl_2

Large amounts of S_2Cl_2 remain to be removed from solids following the liquid/solids separation steps. This must be done by volatilization, requiring large volumes of carrier gases (N_2 and excess Cl_2), from which S_2Cl_2 must be extensively recovered for recycling. Residual S_2Cl_2 must then be fully removed, for example by water or alkaline scrubbing of tailgas, since S_2Cl_2 cannot safely be emitted to atmosphere. These operations are likely to be complicated and expensive.

Advantages of Process

Potential advantages of the process should also be mentioned.

Low temperature chlorination and related process steps in S_2Cl_2 environment are carried out in a temperature range where known materials of construction could be used (austenitic stainless steel and Monel are suggested in the Peters patent). A comprehensive program of tests would however be needed to determine which economically accessible materials of construction (metallic and non-metallic) stand up to S_2Cl_2 in combination with abrasive materials (gangue) and dissolved sulphur. In any case, corrosion problems should be easier to solve than for the higher temperature alternatives.

The crystallized sulphur could require several purification steps in order to produce a marketable product. The primary product might contain a substantial amount of S_2Cl_2, as indicated by 75-80% S in crystallized sulphur (verbal information from CANMET). The behaviour of impurities which could report in the sulphur, such as Se, Te, As, etc. would have to be investigated in order to define further purification steps which might be required.

The patent literature indicates that the process is in principle applicable to a wide range of copper and nickel sulphides and pyrite, besides the zinc-rich complex Zn-Cu-Pb-FeS_2 concentrates on which most of the reported test work has been carried out.

PRINCIPLE OF PROCESS

The pyrometallurgical part of this process can be summarized as follows.

Chlorination

Dried sulphide concentrate is chlorinated with S_2Cl_2 recycled from sulphur removal and S_2Cl_2 regeneration. The general reaction is:

$$MS + S_2Cl_2 \rightarrow MCl_2 + 3\ S$$

Copper, however, appears to form cuprous chloride (CuCl) and iron goes partly to $FeCl_2$ and partly to $FeCl_3$. Consequently, the following chlorides are present in the reaction product:

$ZnCl_2$
$PbCl_2$
CuCl
AgCl
$FeCl_2$
$FeCl_3$

The formed sulphur is dissolved in excess S_2Cl_2 (at least 5 times stoichiometric is suggested). The resulting solids therefore consist of the above chlorides and unreacted sulphides.

The effects of temperature and time on metal extractions are not clear from the test results. The suggested preferred range is 80-100°C with 30-60

minutes retention time.

Liquid/Solids Separation

The solids (chlorides and residual sulphides) are separated from the S_2Cl_2-S° solution. Complete removal of S_2Cl_2 and S° from the solids is required prior to further hydrometallurgical processing, because:

1. S_2Cl_2 reacts with water to HCl, H_2S, SO_2, and S°.
2. Sulphur coating of solid particles reduces their leachability.

A "drying" operation is therefore proposed, to remove excess S_2Cl_2 by volatilization with nitrogen as carrier gas, and with chlorine to convert dissolved sulphur to S_2Cl_2. The sulphur monochloride is condensed and recycled to chlorination.

Sulphur Recovery

Sulphur is recovered from the S_2Cl_2 solution by cooling and crystallization; S_2Cl_2 is then recycled to chlorination.

Sulphur Monochloride Regeneration

The amount of chlorine in S_2Cl_2 converted to metal chlorides must be regenerated by reacting sulphur with chlorine gas recycled from the hydrometallurgical plant where Cl_2 is recovered anodically from electrowinning of Pb, Cu and Zn.

EXPERIMENTAL BASIS

Test work sponsored by CANMET is described in reports by Weatherell[2] and Salo.[3] Only small scale laboratory batch tests have been carried out, ranging from 5 to 25 g concentrate per batch. The reaction is exothermic and temperature rose during the batch tests, reaching a maximum of 79 to 116°C. All these tests were performed on a complex Zn-Cu-Pb concentrate from New Brunswick.

The Peters patent[4] concerns pyrite treatment with S_2Cl_2; examples in it refer to temperatures up to 140°C. The Fonseca patent[5] describes a similar process for chalcopyrite at 100°C and pentlandite at 80°C. A Russian paper[6]

describes tests ranging from 50 to 130°C, based on application to complex Zn-Cu-Pb sulphide concentrates.

Thus, most of the experimental data available refer to Zn-Cu-Pb concentrates from complex, pyritic sulphide ores such as those found in New Brunswick. The Fonsica patent[5] claims that Cu can be extensively (93%) solubilized from chalcopyrite at 100°C, and Ni substantially solubilized from pentlandite at 80°C by treatment with S_2Cl_2. Information provided in the examples is however very sketchy. Fonsica extracted the metal values from the S_2Cl_2 reaction product by leaching with ammonium hydroxide-chloride solutions.

Information available from small scale batch laboratory tests therefore indicates that the low temperature S_2Cl_2 process is in principle applicable to a wide range of complex concentrates containing zinc, copper, lead and nickel sulphides, as well as pyrite.

PRACTICAL APPLICATION OF PROCESS

The main process steps and their application to a commercial plant, are commented upon below. These comments are limited to the chlorination process, while the subsequent hydrometallurgical process for recovery of the metal values, is commented upon in a separate section of this report.

Concentrate Drying

The concentrate must be dried to a low moisture content (say <0.1% H_2O) since S_2Cl_2 reacts with moisture. It might be desirable to remove air entrapped in the dried concentrate, to avoid air ingress into the sealed process system. Drying and purging could be carried out in fluid bed units.

Chlorination

The chlorination step might be carried out in a series of agitated tanks, equipped with refluxers to control S_2Cl_2 volatilization (BP: 138°C). Concentrate could be added through a gas tight double bell feed system. A fairly large S_2Cl_2 recycle volume, say 5-10 times the stoichiometric amount required for metal sulphides conversion, is probably needed to achieve a sufficiently high liquid/solids ratio in the slurry, so that it could be handled

through the system, particularly in view of S_2Cl_2 viscosity, which is considerably higher than that of water, and which increases with dissolved sulphur content, as shown in the table below taken from Gmelin (fig. 400, p. 1751):

Viscosity in Centipoises

°C	water	S_2Cl_2	S_2Cl_2 with 26% S
0	1.8	12.7	30
10	1.3	11.2	24
20	1.0	10.0	21
40	0.66	9.0	18

It is difficult to visualize a batch process because this would require emptying and refilling reaction tanks under gas sealed conditions, or using large volumes of purging gas from which S_2Cl_2 would have to be removed before expelling batches of purge gas to atmosphere.

The chlorination step must therefore be a continuous operation. Countercurrent operation cannot be seriously considered as this would require several difficult liquid/solids separations within the chlorination step itself. Consequently, the most feasible way to visualize the chlorination step is as a continuous concurrent operation in a cascading series of tanks.

Liquid/Solids Separation

Decantation, as suggested in the Peters patent, is unlikely to be sufficient by itself, since the decanted solids will still contain a significant quantity of S_2Cl_2 with dissolved S, amounting to more than the solids by weight according to Example 1 in the Peters patent, which all would have to be removed in the subsequent drying step.

The most practical approach is a battery of batch pressure filters operating on a fully automated cycle, of which at least one will always accept the continuous slurry stream from the last chlorinator. It is suggested that L/S separation, drying and purging could all be carried out sequentially in the same pressure filter.

Drying and Purging of Chlorination Residue

Drying tests (removal of S_2Cl_2 by volatilization) have been carried out on chlorination residue, using N_2 or $N_2 + Cl_2$. Both gases would have to be completely dried before use. Two requirements stand out:

1. Dilution with Nitrogen

   Very complete removal of S_2Cl_2 is necessary as this toxic compound cannot be allowed into the leaching and subsequent "open" hydrometallurgical operations, and also because S_2Cl_2 reacts with water to HCl, H_2S, SO_2 and elemental sulphur which coats the solids and thus prevents extraction of the metal chlorides.

   To ensure this complete removal we have included two stages: "drying" and "purging". Similarly, two stages of S_2Cl_2 removal by "distillation" are proposed in Peters' patent.

   Physical data available for S_2Cl_2 indicate the minimum volumes of diluent gas (nitrogen is suggested) required to satisfy S_2Cl_2 partial pressure:

   at 80°C: 5.3 times S_2Cl_2 volume
   at 100°C: 2.1 times S_2Cl_2 volume

   In practice, higher dilutions are required for effective drying under practical conditions. Even assuming that purging step offgas would be recycled to the drying step, it seems reasonable to expect that 5-10 times the driven-off S_2Cl_2 volume would be required to ensure effective drying under practical conditions.

2. Chlorine Addition

   A significant amount of dissolved sulphur will reach the drying step with the wet solids from L/S separation; this amount of sulphur would be particularly high if decantation turns out to be the only practical L/S separation method.

This sulphur must be completely removed to avoid S-coating of residue, which prevents effective metal extractions in the subsequent aqueous leach operation. Consequently, sufficient Cl_2 gas must be added to the drying step to completely convert this S to S_2Cl_2.

Consequently, one must visualize a large volume of nitrogen being fed to the purging step, and from it back to the drying step with some chlorine added. The drying step offgas will therefore consist of a large volume of N_2 + S_2Cl_2 + excess Cl_2.

Weatherell showed in small tests that a substantial amount of S_2Cl_2 can be driven off with N_2 at 90°C. Similar tests by Salo at 69°C with N_2, and with N_2 + Cl_2 indicate that S_2Cl_2 removal is incomplete at this lower temperature. These tests removed up to 55 weight % of the wet (i.e. unseparated) chlorinated ore and presumably assumes that the removed weight is mainly excess S_2Cl_2. The tests were performed on 3 g samples at up to 60 min. in a stream of 130-140 cm^3/min. N_2, corresponding to 5.5 times theoretical at 80°C; 10-20 cm^3/min. Cl_2 was added to the above nitrogen volume.

It has been suggested that a solvent such as CS_2 could be used for the "drying" step, i.e. for removal of excess S_2Cl_2 from the chlorination residue. The solvent would at the same time remove sulphur dissolved in the S_2Cl_2. Subsequently, however, it would be necessary to separate S_2Cl_2 + S° from the solvent; this would require handling of a health hazardous solvent on a substantial scale in a completely enclosed system. Without further test work followed by conceptual design studies it is not possible to give an opinion as to which alternative would be preferable - "drying" with nitrogen carried Cl_2, or solvent washing. In the latter case, the recovered S_2Cl_2 + S° would also have to be rechlorinated before joining the main S_2Cl_2 recycle stream.

Sulphur Crystallization

The literature, as summarized in Gmelin, gives contradictory data on the solubility of S in S_2Cl_2, which seems to vary with S_2Cl_2-S solution preheat temperature. When cooling from 100°C, i.e. corresponding roughly to the

proposed chlorination temperature, the following weight % S solubilities are shown (Gmelin, fig. 398, p. 1750):

°C	approx. weight % S in liquid
100	95
90	85
80	78
70	72
60	64
50	57
40	45
30	38
20	32
10	18
0	15

According to the Peters patent, S_8 solubility in S_2Cl_2 is:

°C	mole % =	weight %
65	40	56
58	32	47
41	20	32

but these data seem to correspond to those for starting with cold S_2Cl_2 which, according to information in Gmelin, are quite different. In other words, considerably higher sulphur solubility is measured when the hot solution is cooled; this is explained by the stability of supersaturated solutions of sulphur in S_2Cl_2. Whatever the theoretical reason for this behaviour of such solutions, the supersaturation phenomenon is likely to interfere with the practical aspects of recovering sulphur by crystallization from such solutions.

In practice, it means that a solution with 26% S, which still has about 20 times the viscosity of water, will require cooling to <10°C in order to crystallize a significant proportion of the sulphur. One must therefore visualize operating chlorination at a reasonable S-level, and say 5 to 10 times stoichiometric S_2Cl_2 amount, removing a bleed stream to cooling and crystallization while most of the S_2Cl_2-S solution is recycled directly to chlorination, as shown on the flowsheet.

S_2Cl_2 and S are miscible in any proportion above the melting point of sulphur, and sulphur solubility is obviously still very high (78-95%) in the 80-100°C chlorination temperature range. Such a concentrated solution probably becomes very viscous when cooled for crystallization and the above described mode of operation would therefore seem to be required.

Cooling might require agitation to avoid sulphur deposition on cooling surfaces. Maybe vacuum removal of a proportion of the S_2Cl_2 would be the best way to cool and concentrate the solution and at the same time keep S-crystals in suspension. The best way to separate the crystals and remove adhering S_2Cl_2 would be by centrifuging, followed by vacuum drying.

The high solubility of sulphur and high viscosity of S_2Cl_2-S solutions indicate that solution cooling, sulphur crystallization, separation and drying (i.e. complete removal of residual S_2Cl_2 from the crystals) are likely to be difficult operations to perform on industrial plant scale.

In test reports made available to us by CANMET, we have not found any figures concerning S_2Cl_2-sulphur separation but have been informed verbally that the separated sulphur contained 75-80% S. This indicates a significant amount of S_2Cl_2 intimately connected with the sulphur in some way, whether in solid solution or as a viscous film on the sulphur crystals.

Differences in specific gravity are shown below (Gmelin, fig. 399, p. 1751):

S_2Cl_2, pure	1.71 at 0°C (1.65 at 40°C)
S, rhombic	2.07
S, monoclinic	1.96
S_2Cl_2 with 26% S	1.76 at 0°C (1.72 at 40°C)

The difference seems insufficient to achieve good settling but should be adequate for centrifuging, unless the slurry proves difficult to handle on account of its viscosity.

S_2Cl_2 Regeneration

No C-I-L work was directed at this question but information in H. W. Parsons' CANMET report MRP/MSL 76-185(TR) of July 1976 states that S_2Cl_2 is

commercially manufactured by sparging of Cl_2 into liquid S_2Cl_2 to which elemental S is added. The reaction is exothermic and requires cooling to below 50-60°C to avoid formation of SCl_2. From this we assume that regeneration of S_2Cl_2 can easily be carried out commercially from S and Cl_2 at say 40°C. The problem is how to cope with the large volumes of nitrogen from the chlorination residue and crystallized sulphur drying and purging steps. One can visualize that most of the S_2Cl_2 could be condensed from these gases by cooling to say 10-20°C. The remaining gas, consisting of N_2 + Cl_2 + a small amount of residual S_2Cl_2, could be recycled to the chlorination product purging and drying steps.

Condensed S_2Cl_2 from these offgas cooling operations, would serve as medium for regenerating the necessary S_2Cl_2 from recycled chlorine and a proportion of the elemental sulphur recovered from the S crystallization step.

Offgases to Atmosphere

Theoretically, the process could be operated with a balance of S_2Cl_2 circulating through the system. In practice, however, some excess nitrogen purging-drying gas and other lesser streams containing S_2Cl_2 would have to be dealt with before they can be safely emitted to atmosphere. An installation for treating such tail gases for complete S_2Cl_2 removal is therefore required.

S_2Cl_2 reacts strongly with water. One can therefore assume that it can be effectively removed and destroyed by wet scrubbing. The S_2Cl_2 + H_2O reactions produce however a number of undesirable compounds, including H_2S, SO_2, HCl and elemental S. These can all be effectively removed by scrubbing with caustic but the resulting solution would contain chlorides, sulphides and possibly also polysulphides and sulphite. Its treatment and safe disposal to the environment could be complicated and expensive. Consequently, offgases containing S_2Cl_2 must be kept at a minimum. Nitrogen, needed for purging and as S_2Cl_2 carrier for chloride drying, must therefore be recirculated to the fullest extent. In practice, it seems however unavoidable to bring in a small amount of nitrogen (or air) with the dry concentrates.

CHLORINATION PRODUCT AND LEACH EXTRACTION

Physical Nature of Chlorination Product

The Salo report states that the chlorination product is extremely hygroscopic. This could create serious problems for the handling, intermediate storage, and feeding of this material to the leaching step.

Available Test Result Data

In the tests reported to date by Weatherell[2] and Salo,[3] the chlorination product (following excess S_2Cl_2 removal with CS_2) and leach residue were not analyzed. Consequently, no direct information is available on residual sulphide and elemental S content of these materials. The only materials analyzed were the concentrate itself and the leach solutions, from which the leach extractions were calculated.

Chlorination Conditions and Leaching Results

Weatherell[2] and Salo[3] used the following range of chlorination temperatures and retention times (reference is made to diagrams and tables in these reports).

Weatherell

Fig. 1 - Chlorination for 1 hour at 49-90-130°C.

Fig. 2 - Initial temperature 40°C, rising to a high but unspecified temperature due to heat of reaction; extractions determined after 30-60-90 minutes.

Results are summarized below:

	Maintained 1 hr at temp.		Initial 40°C → ∿67°C	
	at 90°C	at 130°C	1 hr.	1½ hr.
Fe tot	83	86	27	49
Fe 3+	59	73	16	26
Cu	95	86	99	99
Zn	73	81	32	35
Pb	62	50	73	70

Salo

Salo varied a number of chlorination conditions, including:

Fig. 3 - Chlorination at 100°C; effect of retention time (20-30-40-60 minutes).

Fig. 4 - Effect of liquid/solid ratio on chlorination (2.5 to 12.5 grams conc. per 30 mℓ S_2Cl_2).

Salo ran optimization tests to determine the effect of liquid/solid (i.e. S_2Cl_2/conc.) ratio in the chlorination step on subsequent leach extractions. The results show that a weight ratio of at least 4 liquid:1 solid is required to ensure maximum Cu and Pb extractions, thus confirming that a large S_2Cl_2 recycle volume is required.

Maximum metal extractions obtained by Salo, using liquid/solids ratios of 4 to 6 (5 to 7.5 g conc/30 mℓ S_2Cl_2) in the chlorination step, gave the following totals for both leaching steps (i.e. water + brine leaches) shown in Table 3.

	% extraction
Fe tot	51 - 56*
Fe 3+	38 - 46*
Cu	101 -103*
Zn	27 - 30*
Pb	93 - 99**

* mostly by water leach

** of which 53-55% by water leach, and additional 40-44% by brine leach.

Note: temperature and retention time not specified, but were probably 100°C and 1 hr. as in Table 5.

Both Weatherell and Salo carried out leaching at ambient temperature, in two stages:

1. with water
2. with 3N NaCl brine.

The following batch leaching times were used (minutes):

	Weatherell	Salo
Stage 1	30	20-120
Stage 2	30	20-120
	60	40-240

Interpretation of Test Results

These results indicate that:

1. High Cu and Pb extractions are possible.
2. Most of Zn remains insoluble, presumably as less reactive ZnS, unless combining high temperature and long retention time in the chlorination step.
3. A large proportion of iron is solubilized, mostly as $FeCl_3$, but also a significant amount as $FeCl_2$.

The extraction diagrams shown in the Weatherell report indicate that Zn might be more effectively chlorinated at higher temperature (73% at 90°C and 82% at 130°C after 1 hour) but the two diagrams on Fig. 1 and 2 of that report seem contradictory on this point, and it therefore seems difficult to draw any conclusions from these. The Salo data give a more coherent picture, and we are therefore basing our comments on Salo's results.

Comments follow regarding the significance of high iron and low zinc solubilities.

Iron Solubility

A complex concentrate usually contains much iron, partly as pyrite which reacts with S_2Cl_2. Most of the iron reports as soluble iron chlorides in the chlorination product; this includes a high proportion of ferric chloride. In the Salo optimization tests (Table 3), the figures show that 74-82% of total extraction iron was Fe^{3+}.

In the Peters patent it is claimed that pyritic iron mainly goes to ferric chloride according to the reaction:

$$3\ S_2Cl_2 + 2\ FeS_2 \rightarrow Fe_2Cl_6 + 10\ S^\circ$$

This occurs at higher temperature (135-145°C) as shown in Example 1 of the patent.

The net amount of sulubilized iron must somehow be removed from the hydrometallurgical circuit in an environmentally acceptable form. Without discussing the hydrometallurgical process in detail at this point, it is evident that the iron would be removed in one of the two following ways:

1. Precipitation as a ferric hydroxide or oxide, by oxidation of ferrous iron and hydrolysis.

2. A more complicated way would be to produce a concentrated pure $FeCl_3$ solution by solvent extraction (as done in Société Le Nickel's nickel refining process) and use that solution for re-leaching primary leach residue at higher temperature for additional zinc extraction. There exists a limited market for $FeCl_3$ for water purification but iron could not be disposed of this way on a large scale. Furthermore, it would require a correspondingly large amount of make-up chlorine.

Iron can thus be removed by one of the methods which would be used in proposed hydrometallurgical chloride processes for complex sulphides. The latter processes only solubilize iron contained in reactive sulphide minerals, such as chalcopyrite, marmatite and pyrrhotite, whereas dry chlorination also solubilizes pyritic iron and therefore increases the magnitude and cost of the iron removal step. It indicates that, from an economic viewpoint, the application of this process should be limited to complex sulphides with low pyrite content.

Zinc Solubility

It is well known that zinc in ZnS can be solubilized by leaching with $FeCl_3$ solution, according to the reaction:

$$ZnS + 2\ FeCl_3 \rightarrow ZnCl_2 + 2\ FeCl_2 + S$$

To avoid ferric iron in the resulting leach solution, 2-stage countercurrent leach at 100-105°C can be used, as for example in the Elkem process.

Consequently, we believe that a high zinc extraction and recovery could be achieved in practice by a 2-stage countercurrent leach of the chlorination product at 100-105°C. If the $FeCl_3$/residual ZnS ratio in the chlorination product is not sufficient to satisfy the above equation, then $FeCl_3$ solution could be recycled to the leach from the hydrometallurgical circuit, following recovery of valuable metals and elimination of an amount of iron corresponding to that introduced with the chlorination product.

HYDROMETALLURGY

A suitable hydrometallurgical process for the chlorination product would generally follow the same lines as direct ferric chloride leaching processes already investigated by CANMET, USBM, Elkem and others, of which some have been tested on pilot plant scale in recent years.

Such a process is briefly described in general terms below.

Leaching

The chlorination product would be leached in a 2-stage countercurrent system at 100-105°C, to ensure complete reduction of $FeCl_3$ to $FeCl_2$ by excess sulphides (mainly ZnS) in the second leach stage. Excess $FeCl_3$ present in the first leach stage completes the reaction of non-ferrous sulphides remaining in the Stage 1 leach residue.

If the chlorination product contains less $FeCl_3$ than required for conversion of ZnS and other reactive sulphides in the chlorination product, then the deficient amount would be provided by recycling $FeCl_3$ solution regenerated from the tail solution following non-ferrous metals extraction.

If an excess of $FeCl_3$ is introduced with the chlorination product, then this should be reduced before silver recovery and zinc extraction, and preferably even before lead removal. The most economical way to achieve this is probably to add the needed quantity of sulphide concentrate directly to the leach. This situation would arise, for example, if high zinc conversion is achieved in the chlorination step so that little ZnS is present in the chlorination product to leaching.

Following this, the slurry would be filtered, the rejected residue consisting mostly of gangue, elemental sulphur and residual metal sulphides including some unreacted pyrite.

Lead Removal and Recovery

The solution is cooled to 25-40°C, to crystallize out a proportion of $PbCl_2$ corresponding to incoming lead. $PbCl_2$ is separated, dried and lead recovered from it by fused salt electrolysis. This has been piloted by USBM, Hazen Research, Alcoa and others.

Copper is removed by solvent extraction (Elkem-ICI technology or similar) and recovered by electrowinning from chloride solution, provided there is sufficient copper in the concentrates to justify separate copper recovery.

For concentrates with low Cu content, the copper could be cemented out together with silver as described below.

$FeCl_3$ Reduction and Silver Recovery

While most of the iron is present as $FeCl_2$, a small amount of $FeCl_3$ is likely to still be present in the solution. Residual Fe^{3+} is then reduced and silver precipitated by cementation with Zn powder.

All the iron is now present in the solution as $FeCl_2$, as required to avoid iron transfer in the subsequent zinc removal step.

Zinc Removal and Recovery

Zinc is removed by solvent extraction with TBP and recovered by electrowinning in chloride solution, as piloted on small scale by Elkem. The zinc electrowinning circuit will require purification of the zinc strip solution including iron removal and precipitation of Cu and other minor impurities with Zn powder, as in a conventional electrolytic zinc plant.

Iron Control and Removal

Following zinc removal the solution contains all iron as $FeCl_2$. This is oxidized by heating to ~80°C, sparging air or oxygen to remove the amount of iron corresponding to the soluble iron content of the incoming chlorination product. One-third of the ferrous iron is removed, corresponding to the reaction:

$$6\ FeCl_2 + 1\tfrac{1}{2}\ O_2 \rightarrow Fe_2O_3 + 4\ FeCl_3$$

Actually, iron is precipitated as akaganeite (FeOOH), according to Elkem.

General Circuit

To achieve the desired concentrations, such as of $PbCl_2$ for example, some steps may be carried out in recirculated solution or bypass loops within the overall circuit. Where, and to what extent this is required, will depend on the composition (relative Pb-Cu-Zn-Fe contents) of the complex concentrate.

Modest additions of acid and alkali may be required to adjust the solution to the pH required for the various steps. This would presumably be done with HCl and NaOH to avoid bringing other ions into the system. It would result in some accumulation of NaCl which would have to be controlled by a bleed stream of barren solution to waste. This would at the same time control minor impurity accumulation.

Chlorine gas from Pb, Cu and Zn electrowinning must be cleaned and dried before recycling to the chlorination step.

FUTURE TEST WORK PROGRAM

Our negative conclusions are in part based on the results of small scale tests carried out to date. However, some of these results are either inconclusive or difficult to interpret. In the event that CANMET should decide to carry out further exploratory tests before deciding whether the low temperature chlorination route should be pursued or definitely abandoned, we recommend that additional small scale tests should be carried out in the following areas.

1. Determine conditions governing $FeCl_3$ vs $FeCl_2$ formation in the chlorination step. The influence of variables such as temperature and S_2Cl_2 excess should be investigated. The mineralogical association of Fe (i.e. as pyrite vs other Fe containing sulphides) is also of interest. Comparative tests could be made on Brunswick complex concentrate and a pyrite concentrate.

2. Determine ZnS (sphalerite) reactivity as function of $FeCl_3$ present in the chlorination step. One suspects that ZnS might require $FeCl_3$ for chlorination in the 80-100°C temperature range since CANMET has already determined that pure ZnS (sphalerite and chemical reagent grade) does not react directly with S_2Cl_2.

3. Determine reactivity of S_2Cl_2 as function of dissolved S content. Batch tests could be carried out, using S_2Cl_2 with various S levels, preferably reaching indicated recycle stream levels (say 35-60% S).

4. Carry out tests on crystallization of sulphur from solutions of $S-S_2Cl_2$, by cooling say 35-60% S solutions from chlorination temperature (say 100°C) down to say 10-20°C.

5. Observe the physical characteristics (viscosity, settling, etc.) of chlorination product and sulphur crystallization slurries in connection with 3. and 4. above.

The above small scale test program should clarify some of the factors which seem uncertain at present.

It would be premature to outline a program for further tests before the results of the above test program have been obtained. It is evident, however, that any further test program would require considerable time and expenditure as it would at some point require continuous operation, with major recycle streams, in an environment and under conditions which are largely unknown at present.

SOURCES OF INFORMATION ON LOW TEMPERATURE CHLORINATION PROCESS

1. G.M. Ritcey, C.J. Weatherell, R. Molnar, S.A. Salo: "A Low Temperature Process for the Chlorination of Complex Base Metal Sulphides using Sulphur Monochloride", paper prepared for AIME Annual Meeting, Los Angeles, Feb. 1984 (covers also medium temperature process).

2. Carl Weatherell: "Chlorination of Sulphide Ores, with Sulphur Monochloride", EM&R Canada report, Ottawa, August 1983.

3. S. A. Salo: "Investigations into the Chlorination of Sulphide Ore Concentrate with Sulphur Monochloride", CANMET report No. MSL-INT 84-2.

4. E. Peters, R. McElroy: "Chlorination of Iron Sulphides", Canadian Patent 923,682, April 3, 1973.

5. A. G. Fonseca: "Recovery of Metals from Sulphur Bearing Ores", U.S. Patent 3,979,265, Sept. 7, 1976 (includes example on nickel ore).

6. V. V. Turchaninov, B. M. Reingold, A. S. Sinakevich: "Chlorination of Polymetal Concentrates in Sulfur Monochloride", NRC translation TT-1687, Ottawa 1973, of Russian paper from 1963.

SOURCES OF INFORMATION ON SULPHUR MONOCHLORIDE (S_2Cl_2)

7. R. C. Brastad: "Comprehensive Inorganic Chemistry", D. van Nostrand, New York 1961, pp 92-95. Contains information on:

Chemical properties
Thermodynamic data.

8. "Gmelin's Handbuch der Anorganischen Chemie", 8 Auflage (8th edition) 1963, S-Schwefel (Sulphur), Teil B-lieferung 3 (Part B-subpart 3), pp 1748-1786. In German. Contains a very extensive review of all data on sulphur chlorides published prior to 1963, including:

S_2Cl_2-S and S_2Cl_2-Cl_2 systems
S solubility in S_2Cl_2
Viscosity of S_2Cl_2-S solutions
Vapour pressure
Physical and chemical properties.

9. "Handbook of Chemistry and Physics", CRC Press, 58th edition, 1977-78, page D-187:

Vapour pressure

Specific gravities of S_2Cl_2 and various forms of sulphur are also found in this book.

10. L. F. Doty, CIL Chemicals Research Laboratory: "Development of a Process for Recovering Sulphur from Sulphur Monochloride". Report dated May 13, 1977. It was found that thermal decomposition of S_2Cl_2 is not feasible below 500 or even 1000°C.

S_2Cl_2 - PHYSICAL DATA

Note: Data from Gmelin on solubility of S in S_2Cl_2, and on viscosity of S_2Cl_2-S solutions, are shown in the text.

VAPOUR PRESSURE OF S_2Cl_2

From: Handbook of Chemistry and Physics, 58th Edition, p. D-187.

		Vapour Pressure	
	Temp. °C	mmHG =	atm.
	- 7.4	1	0.0013
	+ 27.5	10	0.013
	54.1	40	0.06
	75.3	100	0.13
	115.4	400	0.6
	138.0	760	1.0
gives by interpolation:	80.0	120	0.16
	100.0	250	0.33

Melting Point: - 80°C

Volume of Diluent Gas Required for Drying

(Theoretical minimum volumes, from nil S_2Cl_2 content to saturation)

@ 80°C: 5.3 x S_2Cl_2 volume

@ 100°C: 2.1 x S_2Cl_2 volume

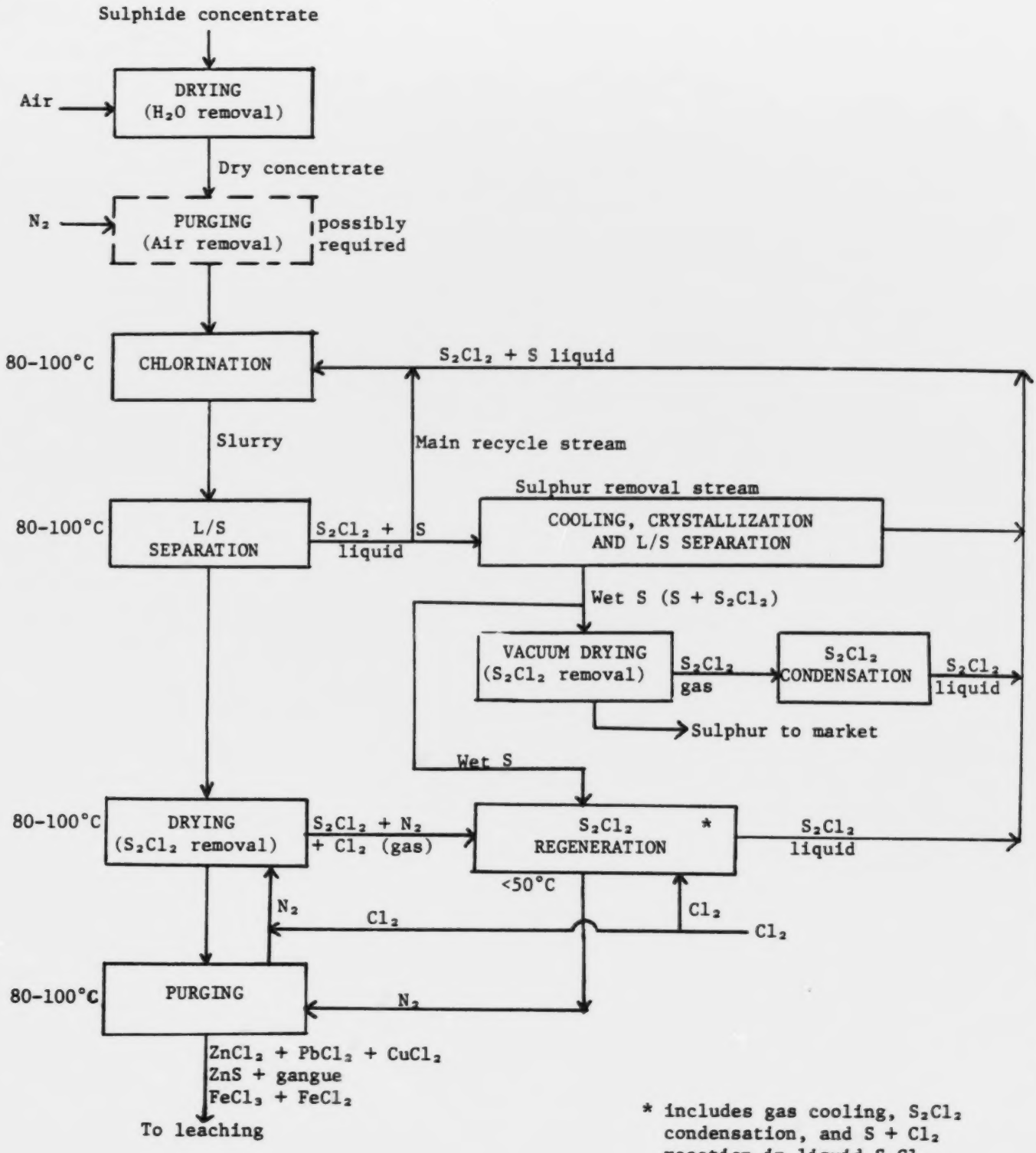
Of course, several times these dilutions are required for effective drying under practical conditions.

SPECIFIC GRAVITIES

S_2Cl_2	1.678
S (rhombic)	2.07
S (monoclinic)	1.96
S (liquid)	1.7988 at 125°C
	1.7947 at 130°C
	1.7865 at 140°C
	1.7784 at 150°C

LOW TEMPERATURE CHLORINATION FLOWSHEET

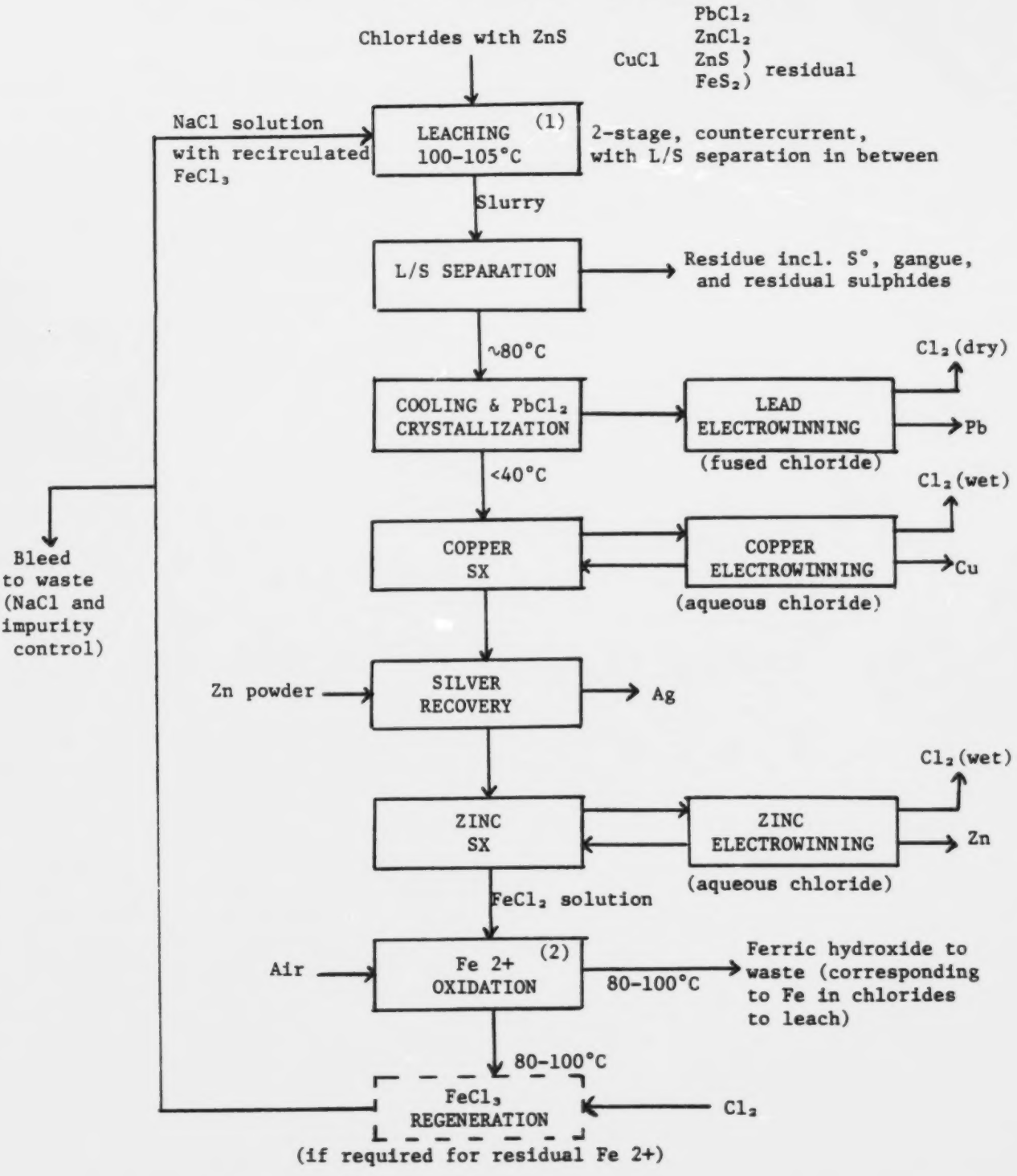
Flowsheet 1: S_2Cl_2 Process Circuit



* includes gas cooling, S_2Cl_2 condensation, and S + Cl_2 reaction in liquid S_2Cl_2

LOW TEMPERATURE CHLORINATION PROCESS

Flowsheet 2: Hydrometallurgical Circuit



REACTIONS

(1) ZnS leaching: $ZnS + 2\ FeCl_3 \rightarrow ZnCl_2 + 2\ FeCl_2 + S^\circ$

(2) Fe^{2+} oxidation: $6\ FeCl_2 + 1.5\ O_2 \rightarrow Fe_2O_3 + 4\ FeCl_3$

MATERIALS TESTED

CANMET's test work was performed on complex high Zn-FeS_2 concentrates with lesser Pb and Cu contents obtained from Brunswick Mining and Smelting Limited (BM&S) ores. The material tested by Westherell and Salo[1][2][3] was a BM&S bulk concentrate of the following composition:

	%
Zn	29.1
Fe	19.2
Pb	8.3
Cu	0.75
S	34.5

Minor impurities are shown in (1), page 8, Table 1.

The Russian paper[6] describes tests carried out on a bulk sulphide concentrate of the following composition:

	%
Zn	28.90
Fe	13.26
Pb	17.57
Cu	0.25
S	27.80

The Noranda pyrite treated in Example 1 of Peters' patent[4] contained 5% Fe_3O_4; presumably, most of the balance was FeS_2.

The examples in Fonseca's patent[5] used chalcopyrite (Example 1) and pentlandite of composition $(Ni, Fe)_9S_8$ (Example 2) but assays were not given.

MEDIUM TEMPERATURE CHLORINATION PROCESS (~300°C)

CONCLUSIONS

We have concluded that medium temperature chlorination is not a practical process, for the following reasons:

1. Elemental sulphur cannot be separated from the reaction mass at 300°C.
2. This sulphur will therefore react with Cl_2 in Step 3, resulting in accumulation of sulphur in the system, without any practical way out for this sulphur.
3. The sticky, pasty reaction mass cannot be handled in any known type of large scale reactor, nor transferred from one process step to another in a system which has to be completely gas tight.
4. Ferrous chloride oxidation must be carried out at considerably higher temperature (at least 450°C) in order to efficiently volatilize and recirculate ferric chloride. It is difficult to visualize a practical method for heating of such a reaction mass from 300 to 450+°C.
5. Any elemental sulphur or metal sulphides remaining in the chlorination product will be oxidized in Step 4 to SO_2, thereby negating the primary objective of the chlorination process, which is to avoid SO_2 emissions.

Our opinion is therefore that the medium temperature chlorination process need not be further looked into and that additional test work is not justified.

PRINCIPLE OF PROCESS

The pyrometallurgical part of this process, as described in CANMET's report MRP/MSL 79-107(IR) of July 1979,[17] can be summarized as follows.

Step 1

Dried sulphide concentrate is chlorinated with S_2Cl_2 recycled from Step 3:

$$MS + S_2Cl_2 \rightarrow MCl_2 + 3\ S$$

Only a part of total sulphides is chlorinated in this step. Consequently, the product from this step is a mixture of metal chlorides, elemental sulphur, excess metal sulphides, and gangue.

Step 2

A proportion of the remaining metal sulphides is chlorinated with ferric chloride recycled from Step 4:

$$MS + Fe_2Cl_6 \rightarrow MCl_2 + 2\ FeCl_2 + S$$

The product from this step is a mixture of the metal chlorides, ferrous chloride, residual metal sulphides, a further amount of elemental sulphur, and gangue.

Step 3

Final chlorination of residual sulphides with Cl_2:

$$2\ MS + 3\ Cl_2 \rightarrow 2\ MCl_2 + S_2Cl_2$$

This step completes the conversion of all metals in the concentrate to chlorides, and generates S_2Cl_2 for recycle to Step 1.

Step 4

Ferrous chloride is converted with oxygen to insoluble Fe_2O_3 and ferric chloride (Fe_2Cl_6):

$$12\ FeCl_2 + 3\ O_2 \rightarrow 2\ Fe_2O_3 + 4\ Fe_2Cl_6$$

Ferric chloride is volatilized and recycled as Fe_2Cl_6 gas to Step 2. The solid product from Step 4 consists of soluble Zn, Pb and Cu chlorides and insoluble gangue and Fe_2O_3, the latter theoretically corresponding to all the iron present in the treated sulphide concentrate. This solid residue goes to leaching for recovery of the non-ferrous metal values.

EXPERIMENTAL BASIS

Chlorination of sulphide minerals at ∿250°C was investigated by H.W. Parsons of the Mine Branch already in 1967.[11][12] Laboratory tests were carried out in rotary glass reactors.

The work was taken up again at CANMET by H.W. Parsons et al in 1975 and test work proceeded for several years, the last report being dated July 1979.[11-17] Experiments were carried out in the 250-500°C temperature range, with most of the test work at ∿300°C. Initial batch tests (1975-1977 reports) were carried out in glass rotary reactors with ceramic balls; areas investigated included chlorination, oxidation of $FeCl_2$ to Fe_2O_3 + $FeCl_3$, chlorination of sulphides with $FeCl_3$, and leaching of chlorination product in water and NaCl brine. The effects of a number of variables were investigated.

In the most recent tests, reported in July 1979,[17] CANMET installed elaborate equipment in attempts to achieve continuous chlorination in a twin-screw reactor at concentrate feed rates of up to 9.1 kg/hour. The tests confirmed that S_2Cl_2 is an effective chlorinating agent in this temperature range and that high percentages (up to 94-96%) of Zn, Pb and Cu can be extracted from the concentrate at 300°C with ½ hour retention time. The tests were nevertheless unsuccessful insofar as the problem of physically transporting the sticky, pasty chlorinated material could not be overcome, so that continuous operation could not be maintained. Besides jamming of the feed and transportation screws, problems were also encountered in the exit gas ducting and cleaning system in connection with sulphur condensation and plugging. Most runs were carried out with Cl_2 only as chlorination gas. Only in some tests was S_2Cl_2 used as chlorination agent, as intended in the 1st step of the proposed process; comparatively low extractions (66% of Pb - 54.6% of Zn - 3.2% of Fe - 0.14% of Cu) were obtained in these exploratory continuous tests with S_2Cl_2, but the S_2Cl_2 added corresponded to only 37.5% of stoichiometric total chlorination requirements; it was calculated that 89% of the added S_2Cl_2 had reacted. This indicates that non-ferrous sulphide minerals (MS) react preferentially to pyrite and that therefore high non-ferrous metal extractions can be expected when sufficient S_2Cl_2 is added.

In this connection it should be noted that CANMET had only one reactor for testing all three chlorination reaction steps, of which only the first uses S_2Cl_2 as chlorinating agent.

PROCESS STEP TEMPERATURES

CANMET proposed to carry out Steps 1 to 3 at about 300°C and CANMET's continuous chlorination test program was based on this temperature level.

However, the H.W. Parsons internal report EMT 68-2 of October 25, 1967[12] concludes that ferrous chloride should be oxidized by air at temperatures above 450°C to give insoluble Fe_2O_3 and volatile Fe_2Cl_6. Even at 450°C, however, about 30% of the original $FeCl_2$ had still not reacted after 1 hour retention time (page 4 of Parsons report). Tests based on chlorinated pyrites gave similar results; 10% of the iron remained as $FeCl_2$ after 1 hour at 450°C. Similar tests at 350°C gave similar conversion to ferric chloride but it was incompletely volatilized so that much Fe_2Cl_6 remained in the reaction residue. Consequently, one must conclude that Step 4 must be carried out at 450°C or more, in order to volatilize and recycle ferric chloride to Step 2.

CANMET also carried out chlorination at 500°C and found that S_2Cl_2 is formed also at this temperature. In other tests, however, it was shown that significant Cu, Pb and Ag losses, in the form of insoluble complex chlorides, occur at chlorination temperatures above 400°C, consequently Steps 1 to 3 should be carried out at less than 400°C. On the other hand, if Step 4 requires 450°C or above, then one must expect these complex chlorides to be formed while the chloride mix goes through Step 4 and these insoluble Cu + Pb + Ag complex chlorides would therefore be present in the final chlorination product to leaching.

BEHAVIOUR OF SULPHUR

Elemental sulphur is formed in Steps 1 and 2 at about 300°C; in other words, below the boiling point of sulphur (445°C at atmospheric pressure). We cannot visualize any practical method by which this molten sulphur could be separated from the pasty mix of chlorides, unreacted sulphides, elemental sulphur and gangue. At this temperature, separation can obviously not be achieved by volatilization of the sulphur; filtering of such a mix seems impossible, particularly in view of the viscosity of sulphur in this temperature range, and also because some of the metal chlorides melt below 300°C. It

therefore appears that elemental sulphur will be carried through to Step 3. There, Cl_2 would presumably react preferentially with this elemental sulphur, to form S_2Cl_2. Thus, sulphur would be recirculated and accumulated in the system, in the form of elemental sulphur going through from Step 1 to 3 and S_2Cl_2 gas returning from Step 3 to Step 1.

Removal of sulphur from the circuit in the form of S_2Cl_2 is not feasible since this compound is very stable and cannot be broken down into sulphur and chlorine at elevated temperatures (450-1000°C), according to C-I-L's report of May 13, 1977.[10]

If, on the other hand, Cl_2 reacts preferentially with residual sulphides, then elemental sulphur would be carried through to Step 4 where oxygen would certainly react with sulphur in preference to $FeCl_2$. In this way the sulphur would finally be discharged from the system in the form of SO_2 and this would negate the principal objective of the process, which is to remove sulphur in elemental form so as to avoid the SO_2 emission problems connected with conventional smelting.

HANDLING OF REACTION MIX

The July 1979 CANMET report[17] states that the product from chlorination at 300°C is a sticky, pasty mass. We cannot visualize a practical method for handling such a material continuously on a large scale. We cannot visualize how a mixture of solid and liquid materials could be continuously reacted with recycled gases (S_2Cl_2, Fe_2Cl_6 and Cl_2) in a continuous double screw conveyor or any other known type of reactor. Nor can we see how temperature control would be achieved, i.e. how heat could be supplied or removed from such a system. Heating or cooling jackets would be ineffective for large diameter reactors of this type, as such a reaction mix is bound to have poor heat conductivity, particularly if containing entrapped recycled gases (S_2Cl_2, Fe_2Cl_6, or Cl_2).

HEATING OF CHLORINATION REACTION PRODUCT

Assuming that Steps 1 to 3 could be carried out at 300°C, it would still be necessary to heat the Step 3 reaction product from 300 to 450°C, the

temperature required for Step 4. For reasons already explained, we cannot visualize how this could be achieved, or how the temperature would be controlled if the Step 4 reaction is sufficiently exothermic to bring the temperature up to the required level.

OTHER POSSIBILITIES OF SULPHUR REMOVAL

If the reaction mass from Step 1 and Step 2 could be cooled and solidified, then it would theoretically be possible to remove elemental sulphur by extraction with suitable solvents or perhaps by grinding and flotation. However, the residual mixture of metal chlorides, unreacted sulphides and gangue would then have to be reheated to 300°C to continue the process. We cannot visualize how the reaction mass from any of these steps could be withdrawn from, and re-introduced into the system for the purpose of sulphur removal at low temperature. Besides the problem of cooling and reheating such a mass on a large scale, there is also the almost insolvable problem of maintaining the gas seal when removing and re-introducing such materials, since the whole chlorination system must obviously be absolutely gas tight.

HYDROMETALLURGY

It would serve no useful purpose to discuss leaching of the final residue (metal chlorides and ferric oxide) and the subsequent hydrometallurgical treatment as we do not consider that medium temperature chlorination is practically feasible.

One could however point out that, even if medium temperature chlorination did work, the subsequent ferrous chloride oxidizing step (Step 4) would yield a product with 10-30% of the iron in the form of ferrous chloride.[12] Regardless of how this iron would be removed from the hydrometallurgical circuit, it would mean a substantial loss of chlorine from the pyrometallurgical circuit, which would have to be replaced as chlorine gas, presumably from a caustic-chlorine plant. At the same time, this excess chloride ion would have to be removed from the hydrometallurgical circuit, and this would create a serious effluent disposal problem.

MEDIUM TEMPERATURE CHLORINATION PROCESS

SOURCES OF INFORMATION

11. H. W. Parsons: "Chlorination of Pyrite", EM&R Internal Report EMT 67-16, October 1967.

12. H. W. Parsons: "Chlorination of Zinc-Bearing Sulphide Minerals", EM&R Internal Report EMT 67-17, October 1967, Revised January 1968 (EMT 68-2).

13. H. W. Parsons: "Preliminary Investigations into a Proposed Chlorination Process for Complex Sulphides Containing Zinc", May 1975, CANMET Report No. MRP/MSL 75-23(R).

14. W. Petruk and R. G. Pinard: "Mineralogical Investigation of Residues from Chlorination Leaching of Bulk Flotation Zinc Concentrate from Brunswick Mining and Smelting Limited", July 1976, CANMET Report No. MRP/MSL 76-171(IR).

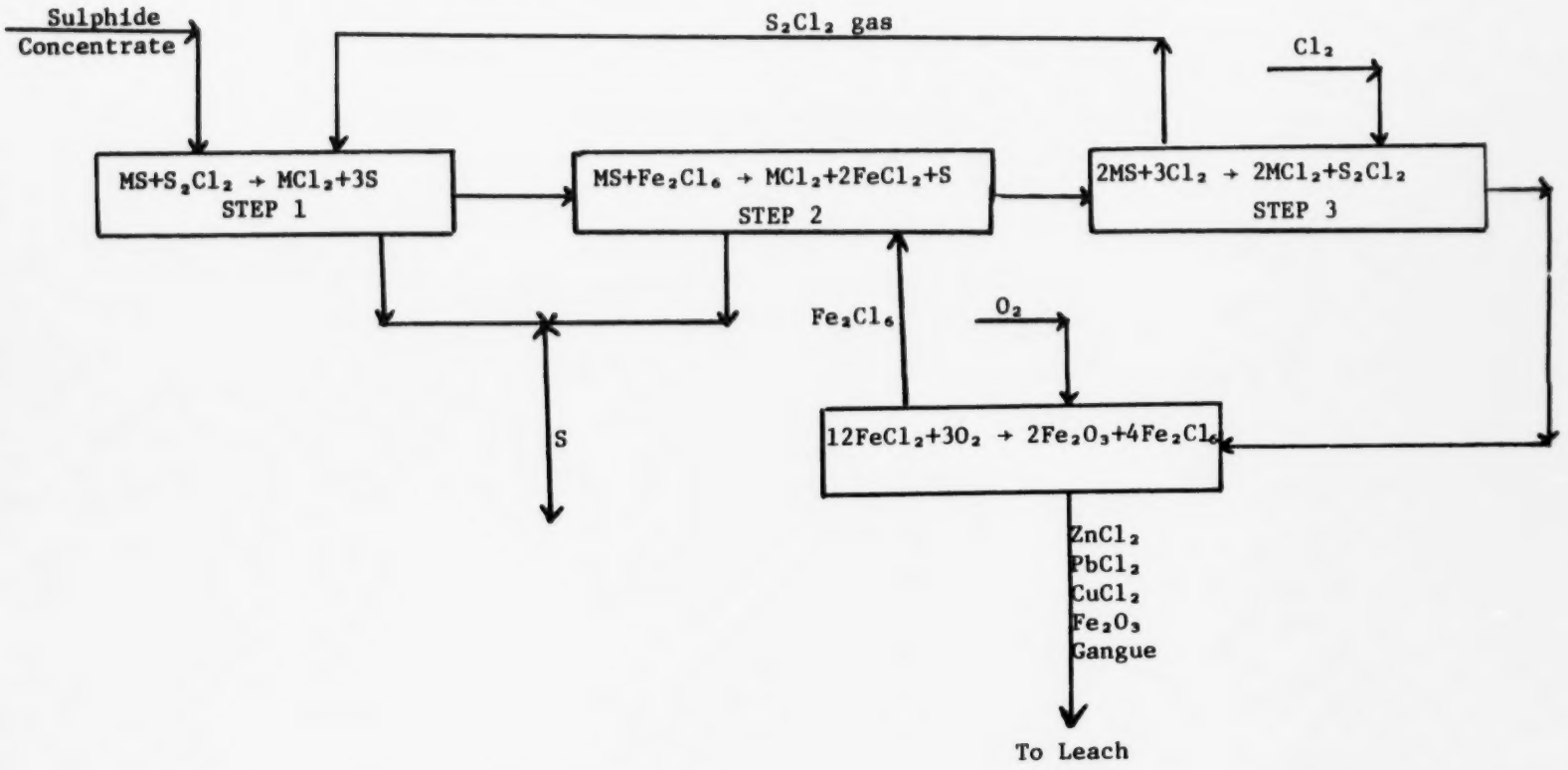
15. H. W. Parsons: "A Discussion of the Disposal of Sulphur Monochloride Produced in the Chlorination of Mineral Sulphides", July 1976, CANMET Report No. MRP/MSL 76-185(TR).

16. H. W. Parsons: "The Dry Chlorination of Zn/Pb/Cu Sulphide Ores;
    1. Investigation of the Chlorination Stage, December 1976, CANMET Report No. MRP/MSL 76-270(IR).
    2. Effect of Diluting the Feed with Iron Oxide, July 1977, CANMET Report No. MRP/MSL 77-127(IR).
    3. Effect of Particle Size, December 1977, CANMET Report No. MRP/MSL 77-128(IR).

17. H. W. Parsons et al: "Low Temperature Chlorination of Zn/Pb/Cu Sulphide Ores Continuous Testing Progress Report No. 1, July 1979, CANMET Report No. MRP/MSL 79-107(IR).

MEDIUM TEMPERATURE CHLORINATION

SCHEMATIC FLOWSHEET



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MATERIALS TESTED

CANMET's test work was carried out on complex high Zn-FeS_2 ores and concentrates with lesser Pb and Cu contents. The most recent work[6][7] was carried out on the following concentrates obtained from Brunswick Mining and Smelting Limited (BM&S) ore.

%	BM&S tailings concentrate	Bulk concentrate prepared by CANMET
Zn	30.17	30.00
Cu	0.69	0.74
Pb	4.00	9.43
Fe	21.97	19.90
S	38.47*	36.60

* shown as 28.47 in (7), page 10 - Table 1, but this is undoubtedly a typing error.

Minor elements are reported in (7), page 11 - Table 2.

A Noranda pyrites concentrate was tested in (1), composition:

	%
Fe tot	45.6
S tot	48.8
S elemental	0.2

HIGH TEMPERATURE CHLORINATION PROCESS (~680°C)

CONCLUSIONS

The high temperature chlorination process avoids to a large extent, but probably not entirely, problems connected with sulphur chloride. It also offers the advantage of recovering the iron in the form of an iron oxide product which might be suitable for marketing or safe disposal, if required physical characteristics and chemical purity can be achieved.

On the other hand, this process also presents a number of practical problems which are briefly outlined below.

Sulphur Chloride Formation

In practice, excess chlorine will be needed to ensure maximum conversion to chlorides; this will produce sulphur chloride (S_2Cl_2) in the offgas which, together with volatilized metal chlorides and excess Cl_2, will make this gas very difficult to treat. These compounds may have to be destroyed by say alkaline scrubbing, at considerable cost, as well as some loss of sulphur and chlorine. This gas stream can be limited by two-stage chlorination but still remains a problem.

Temperature Control

The first chlorination stage might be operated autogenously, if little nitrogen is used, and if chlorine, nitrogen and concentrate are preheated. The second chlorination stage and deferrination require however substantial nitrogen dilution and are expected to be heat deficient in practice. Providing auxiliary heat to these reactors in a practical fashion is likely to be difficult.

Volatile Metal Chlorides

The handling and cleaning of gases containing $ZnCl_2$ and $FeCl_3$ are likely to present practical problems likely to be very difficult to solve in practice. Condensation and handling of liquid $ZnCl_2$ and solid $FeCl_3$ will also

be difficult. These chlorides are likely to deposit as scale on the inner surfaces of a gas system which is rather inaccessible to descaling maintenance, due to the toxic and corrosive nature of the gas.

Gas Separation and Chlorine Recycle

The separation of chlorine from nitrogen and oxygen, for the purpose of recycling the chlorine from dechlorination, could prove difficult and expensive because residual traces of solids ($FeCl_3$ and Fe_2O_3) must be completely removed from the gas before cooling and compression for Cl_2 liquefaction. It may prove necessary to scrub and completely dry the gas again before separation, and this could be very costly.

Flow of Solids in Chloride Melt

Settling of solids (gangue and unreacted sulphides) could block or impede the flow of the liquid chloride melt through the chlorination-deferrination circuit which by its nature must be a fully sealed system in which it is difficult to mechanically move these solids if they do not flow naturally with the chloride melt.

Deferrination

The removal of large amounts of iron from a chloride melt by $FeCl_3$ volatilization, as a continuous operation on commercial scale and to a low iron level in discharged chloride product, is likely to be a very difficult operation. We doubt that it is feasible to achieve in a single step the iron reduction assumed in the present materials balance.

Advantages of Process

Potential advantages of the process should also be mentioned.

Problems related to sulphur chloride can probably be limited to a comparatively small gas stream in this process, as opposed to the lower temperature chlorination processes where the separation from sulphur, recovery and recirculation of sulphur chloride present major practical problems.

High conversion of all metals to chlorides seems possible with high

temperature chlorination, with corresponding high recoveries of copper, lead and also zinc from the hydrometallurgical circuit.

Iron can be extensively removed as $FeCl_3$ vapour at high temperature, at least theoretically. It might therefore be possible to provide a low iron chloride feed material to the hydrometallurgical process, where iron control and removal would become very expensive with a high iron chloride feed, as produced in the low temperature chlorination process.

PRINCIPLE OF PROCESS

Our interpretation of the proposed high temperature chlorination process can be summarized as follows.

Chlorination

Dried sulphide concentrate is chlorinated with Cl_2 to form molten metal chlorides and sulphur vapour. A chlorination temperature of ∿680°C is chosen to produce a fluid chloride bath while minimizing Fe volatilization and limiting $ZnCl_2$ fuming. Chlorine is added with nitrogen as carrier gas for the sulphur.

The chlorination products are consequently:

1. A liquid mix of $PbCl_2$, CuCl, $ZnCl_2$, AgCl, $FeCl_2$ and $FeCl_3$, entraining a small amount of solid gangue and residual sulphides.
2. A gas consisting mainly of N_2 and S_x, with $ZnCl_2$ and a small amount of $FeCl_3$ vapours. Sulphur chlorides are also likely to be present.

Deferrination

The chloride melt, where most of the iron is present as $FeCl_2$, is treated with additional Cl_2 to convert it to $FeCl_3$ and remove it from the melt by volatilization. Again, nitrogen is used as carrier gas. This step is carried out at ∿525°C where the vapour pressure of $FeCl_3$ is substantial while that of $ZnCl_2$ is still very low.

The deferrination products are:

1. A still liquid mix of chlorides, with low content of iron chlorides, for leaching and hydrometallurgical recovery of non-ferrous metals.

2. Fe_2Cl_6 vapour diluted with nitrogen.

Processing of Chlorinator Gas and Sulphur Recovery

Volatilized zinc chloride is removed by condensation at 450-500°C as liquid $ZnCl_2$, which joins the deferrinated chlorides.

Sulphur is recovered from the cleaned gas by condensation at ∿140°C. The condensed liquid sulphur is purified, if necessary, before solidification to marketable sulphur product.

Sulphur condenser offgas, mainly nitrogen with residual S vapour and probably some sulphur chlorides, is recycled to the chlorinator step.

Dechlorination of Ferric Chloride

Ferric chloride in deferrinator offgas is converted to Fe_2O_3 and Cl_2 by dechlorination with oxygen at 640-700°C:

$$Fe_2Cl_6 + 1\tfrac{1}{2}\ O_2 \rightarrow Fe_2O_3 + 3\ Cl_2$$

The objective is to obtain the following products:

1. Solid, anhydrous ferric oxide for safe impoundment or possible sale.

2. Offgas consisting of N_2, Cl_2 and excess O_2. These components are separated to recover Cl_2 for recycling to chlorination.

Hydrometallurgical Process to Recover Non-Ferrous Metals

The solidified deferrinated chloride mix is dissolved in NaCl brine to solubilize Pb, Cu, Ag and Zn chlorides. The individual non-ferrous metals are separated from the solution and recovered as indicated below.

Lead is separated by crystallization of lead chloride, from which lead is recovered by fused salt electrolysis.

Copper is separated by solvent extraction and copper metal recovered by aqueous electrolysis of the $CuCl_2$ strip solution.

Silver is precipitated by cementation with zinc powder.

Zinc is separated by solvent extraction and zinc metal recovered by aqueous electrolysis of the purified $ZnCl_2$ strip solution.

The end solution requires purification, in particular removal of any iron introduced with the mixed chlorides, before being recycled as NaCl brine to the leaching step.

Anodic chlorine gas from Pb, Cu and Zn electrolysis, is recycled to the high temperature chlorination step.

EXPERIMENTAL BASIS

Test work sponsored by CANMET is described in reports by Parsons and Kearns,[18] Fossen,[21] Brandstatter et al,[22] and Pint and McNamara.[23]

Test work reported by Fossen[21] and Brandstatter et al[22] was carried out at the Ontario Research Foundation, using flash chlorination. Bench scale tests were followed by tests in a flash burner reactor with a test rate capacity of 5 kg solids per hour (83 g/min.). Chlorination efficiencies were determined for Zn, Pb and Fe including the effect of excess chlorine. Theoretical calculations were made to evaluate the effects of $ZnCl_2$ volatilization and gas dilution with excess chlorine and nitrogen on theoretical flame temperature. Burner plugging was the main problem which prevented sustained continuous operation, but individual runs of up to 1-2 hours were achieved. The tests were promising from the viewpoint of high conversion efficiencies but much more work is evidently needed to develop a reliable continuous flash burner with its concentrate and gas feeding systems.

Test work reported by Pint and McNamara describes chlorination tests using submerged lance chlorine injection. Tests were carried out on 125-200 g batches. Again, high chlorination efficiencies were achieved, with conversions of metal to chlorides into the melt of up to 95%. Optimum temperature was

determined to be ~675°C and the reaction was considered to be autogenous. Off gases were cooled for sulphur condensation at 150°C, and further for sulphur chloride removal by refrigeration of residual gas. This paper presents a large amount of theoretical information, calculations and considerations, which have been useful in our review of the high temperature chlorination process.

A paper by Ogawa et al[24] describes the test work on dechlorination of ferric chloride carried out in a 1.2 tonnes per day fluid bed pilot reactor by Toho Titanium Company in Japan. These tests show that dechlorination of $FeCl_3$ to Fe_2O_3 is technically feasible under conditions which have been taken into consideration in the present evaluation of the high temperature chlorination process.

REVIEW OF PROCESS

The most complete information, including theoretical background, is found in CANMET's report "Chlorination of Zn-Pb-Cu-Ag-Fe Sulphide Concentrates Employing Submerged-Lance Chlorine Injection" by P. Pint and V. M. McNamara, May 1982.[23]

It must be emphasized that many of the steps in the conceptual overall flowsheet have not been tested, or are incompletely known from CANMET tests and published information from other sources. Our review is therefore based on a tentative flowsheet and assumptions, neither of which are extensively based on proven facts at this time.

CHLORINATION

Chemistry

Dry concentrate is chlorinated with Cl_2 gas diluted with N_2, acting as carrier gas for volatilized sulphur and metal chlorides, at elevated temperature (say 550-750°C range). Metal sulphides are chlorinated according to the reactions:

$$(Pb,Zn,Fe)S + CL_2 \rightarrow (Pb,Zn,Fe)Cl_2 + \tfrac{1}{2}\, S_2$$

$$(Cu,Ag)_2S + Cl_2 \rightarrow 2(Cu,Ag)Cl + \tfrac{1}{2}\, S_2$$

$$FeS_2 + Cl_2 \rightarrow FeCl_2 + S_2$$

$FeCl_2$ reacts with available excess chlorine:

$$FeCl_2 + \tfrac{1}{2}\, Cl_2 \rightarrow FeCl_3$$

and ferric chloride reacts with unreacted ZnS:

$$ZnS + 2\ FeCl_3 \rightarrow ZnCl_2 + 2\ FeCl_2 + \tfrac{1}{2}\, S_2$$

Elemental sulphur reacts with chlorine to form sulphur chlorides:

$$\tfrac{1}{2}\ S_2 + Cl_2 \rightarrow SCl_2, \text{ and}$$
$$S_2 + Cl_2 \rightarrow S_2Cl_2$$

Other reactions could also occur, such as chlorination of gangue SiO_2 to $SiCl_4$, etc. From this it is evident that the overall reaction system is very complex.

Standard free energies of the above and other relevant reactions are shown in (23), page 7, Fig. 1. The same paper shows on page 10, Fig. 3 the vapour pressure of $FeCl_3$-$FeCl_2$-$PbCl_2$-CuCl-$ZnCl_2$ over a melt such as might be formed in the chlorinator from processing a typical Zn-FeS_2 concentrate from BM&S.

	mole %
$FeCl_3$	6.9
$FeCl_2$	39.1
$PbCl_2$	4.8
CuCl	1.6
$ZnCl_2$	47.6

The effect of temperature on $FeCl_2$:$FeCl_3$ ratio in bath and Fe volatilization is shown in (23), page 37, Fig. 12.

Optimum Chlorination Temperature

Based on these data, CANMET's proposed optimum chlorination temperature of 680°C seems well chosen, as a compromise for achieving the following objectives:

1. Maintaining a fluid bath of molten chlorides; below 650°C sulphide particles are coated with viscous $ZnCl_2$, preventing further reaction.
2. Moderate $ZnCl_2$ volatilization (23), p. 10, fig. 3.
3. Minimum Fe volatilization (23), p. 12, fig. 12.
4. Maximum metal recovery in bath (23), p. 29, fig. 9.
5. High chlorine utilization efficiency (23), p. 34, fig. 10.

A stoichiometric deficiency of Cl_2 could be applied to avoid sulphur chloride formation and thereby simplify elemental sulphur recovery from the chlorinator gas. This however leaves in the chlorinator product unreacted sulphides which are undesirable in the subsequent deferrination step.

Conversely, a stoichiometric excess of Cl_2 could be applied to minimize residual sulphides but the excess chlorine will form sulphur chlorides reporting in the chlorinator gas.

It would of course be ideal to operate exactly at stoichiometry but it is unlikely that this can be achieved in practice. CANMET then consider excess Cl_2 to be the preferable mode of operation.

Definition of Stoichiometry

CANMET define the stoichiometric amount of Cl_2 as that required for complete conversion of metal sulphides in concentrates to:

$PbCl_2$

$CuCl$

$ZnCl_2$

$FeCl_2$

$AgCl$

Consequently, no additional Cl_2 is allowed for $FeCl_3$ and S_2Cl_2 formation.

Chlorination with Cl_2 Deficiency

Chlorination with Cl_2 deficiency would achieve the following:

- Minimize $FeCl_3$ in chlorinator gas to $ZnCl_2$ condensing and sulphur recovery.
- No S_2Cl_2 formation, thereby simplifying sulphur recovery and avoiding S_2Cl_2 recycle to chlorination.

On the other hand, there are the following disadvantages:

- Residual metal sulphides are carried on to the deferrination step. Free energies of reaction indicate that a significant proportion of ZnS and copper sulphides will remain in the material transferred to deferrination.

- Excess Cl_2 required for chlorination of $FeCl_2$ and residual sulphides will produce sulphur and S_2Cl_2 in the deferrinator gas. In the subsequent dechlorination step, these will react with oxygen to produce SO_2 and SO_3 which will further complicate Cl_2 recovery from dechlorinator offgas.

Chlorination with Excess Cl_2

Chlorination with excess Cl_2 would achieve the following:

- Maximum conversion of metal sulphides to chlorides. CANMET data, (6), p. 29, Fig. 9, show ∿92% optimum total metals recovery in bath at ∿650°C but this does not include additional recovery in fume.
- The deferrination and dechlorination steps are simplified by low level of unreacted sulphides in chlorinator product, for reasons already explained.

Disadvantages are listed below.

- Chlorinator gas will contain S_2Cl_2 in addition to S. This S_2Cl_2 must be recycled to the chlorinator in the form of tail gas from S condensation, consisting of $N_2 + S_2Cl_2$.
- Fe_2Cl_6 volatilization will probably increase somewhat but is still low at 1.08 Cl_2 stoichiometry, as shown in (6), p. 57, Fig. 12. $FeCl_3$ level might be prevented from rising much in bath if the latter is in contact with unreacted sulphides in the bottom of the chlorinator.

Preferred Stoichiometry

Some CANMET representatives have expressed the opinion that almost complete conversion of sulphides can be achieved with only slightly more Cl_2 than required for $FeCl_2$ formation, i.e. Cl_2 stoichiometry, as defined by CANMET, slightly above 1. This is explained by unreacted sulphide remaining in the chlorinator chloride bath until converted. Chlorination at a slight Cl_2 excess, say 1.1 stoichiometry or less, would leave only a small amount of ZnS in the

chloride melt going to the deferrinator. It was suggested that under these conditions the chloride melt would contain only 0.5-1.0% S.

DEFERRINATION

Deferrination of the chloride melt is achieved by further chlorination of $FeCl_2$ to Fe_2Cl_6 at a temperature where the latter can be volatilized selectively (i.e. with minimal co-volatilization of $ZnCl_2$), using again nitrogen as carrier gas. The diagram in (23), p. 10, Fig. 3 indicates 0.35 atm $FeCl_3$ vapour pressure over such a chloride bath at the suggested deferrination temperature of 525°C, corresponding to a theoretical N_2 partial pressure of 0.7 atm or 2 times Fe_2Cl_6 volume.

CANMET personnel stated that excess Cl_2, say 2 times stoichiometric, is required for efficient chlorination of $FeCl_2$ to $FeCl_3$. In addition, a small amount of Cl_2 will be required for conversion of residual sulphides, mainly ZnS. Consequently, there will be excess Cl_2 and a lesser amount of sulphur chlorides (corresponding to residual S in chlorinator melt) in the deferrinator gas.

We have assumed that such an excess of chlorine will at the same time convert CuCl to $CuCl_2$. This is important for the subsequent hydrometallurgical treatment of the chlorides.

It has been suggested that one-third of the iron could be converted to Fe_2O_3 in the deferrination step by using oxygen (instead of chlorine), according to the reaction:

$$6\ FeCl_2 + 1\tfrac{1}{2}\ O_2 \rightarrow Fe_2O_3 + 2\ Fe_2Cl_6$$

This alternative was discarded because the deferrinator chloride melt is not likely to flow if containing a significant proportion of fine solids.

Within practical limits of excess Cl_2, N_2 volume, and retention time, deferrination cannot be complete. The deferrination product will therefore contain some residual $FeCl_2$ as well as some unvolatilized $FeCl_3$. Both will affect the subsequent hydrometallurgical processing of the deferrinated chloride mix.

PROCESSING OF CHLORINATOR GAS AND SULPHUR RECOVERY

Gas Cleaning

Offgas, leaving the chlorinator at 680°C, contains N_2, S_x, $ZnCl_2$ and a small amount of Fe_2Cl_6. Using excess Cl_2 stoichiometry in chlorination, the gas is assumed to be free of sulphur chlorides.

Zinc chloride is condensed by cooling to 450-500°C, and transferred as liquid $ZnCl_2$ to the deferrinator chloride melt product. The zinc chloride will probably contain small amounts of $FeCl_3$, $PbCl_2$ and CuCl, carried over as vapour and spray.

Some Fe_2Cl_6 will remain in the offgas from $ZnCl_2$ condensation. To avoid contamination of the sulphur product, this Fe_2Cl_6 should be removed, if possible, in a separate condenser operating at an intermediate temperature between 450 and 150°C; depending on the temperature chosen, the ferric chloride would be collected in liquid or solid form (MP: 304°C).

Sulphur Recovery

The subsequent sulphur condensation should be carried out at ~150°C, the temperature at which molten sulphur has its minimum viscosity. The liquid sulphur may require purification before solidification in a marketable form, such as by prilling.

Recycle of Sulphur Condenser Offgases

This gas consists of nitrogen with a small amount of residual (uncondensed) S vapour. It could be recycled to chlorination, provided further sulphur condensation can be avoided, for example by reheating the condenser exit gas. Otherwise, it could be necessary to incinerate the gas, resulting in fuel consumption and a limited SO_2 emission.

DECHLORINATION

Ferric Chloride Condensation and Conversion to Fe_2O_3 (Dechlorination)

Vapour burners for converting Fe_2Cl_6 containing gases with oxygen will give extremely fine Fe_2O_3 which would be very difficult to collect. CANMET therefore suggested[20] that Fe_2Cl_6 be first condensed from the gas, and solid ferric chloride subsequently converted with oxygen to Fe_2O_3 by some method which would give a granular product or at least a coarser product which could be collected from the gas; fluid bed reactors with cyclones returning Fe_2O_3 fines to the bed was suggested. A dechlorination temperature of 640°C is suggested by CANMET.[23]

The dechlorination reaction:

$$Fe_2Cl_6 + 1\frac{1}{2}\ O_2 \rightarrow Fe_2O_3 + 3\ Cl_2$$

has been investigated by the USBM and Du Pont in the United States, and pilot plant tested by Toho Titanium in Japan.

In the Toho Titanium Company process,[24] piloted in Japan in 1973-1978 at a range of up to 1.2 tonnes per day, Fe_2Cl_6 in gas from an ilmenite chlorination reactor was condensed at 150-170°C as a fine and highly fluid ferric chloride powder. The ferric chloride was mixed with fine Fe_2O_3 and fed to a fluid bed reactor operating at ∿700°C, where pure oxygen or oxygen enriched air was blown through the bed, yielding an iron oxide with about 90% Fe_2O_3 (note: the impure condensed ferric chloride also contained aluminum, manganese and chromium chlorides) and 0.1% Cl. Highest obtained oxygen efficiency was 75% (i.e. 33% excess O_2) but the Japanese expected that 85% O_2 efficiency could be obtained in an industrial reactor.

$ZnCl_2$ vapour contained in the dechlorinator feed gas is likely to report, at least in part, as $ZnCl_2$ in the Fe_2O_3 product, as conversion to ZnO does not occur at that temperature.

The feed gas is likely to also contain a small amount of sulphur chlorides, which will be oxidized to Cl_2 and $SO_2 + SO_3$.

Processing of Dechlorinator Offgas

Even if a method for production of granular or coarse Fe_2O_3 from the dechlorination step should be successfully developed, a significant amount of fine Fe_2O_3 dust is bound to be entrained with the dechlorinator offgas. After removing these solid particles, chlorine must be separated from nitrogen and oxygen by cooling and compression. Recovered Cl_2 is recycled to the chlorination step.

HYDROMETALLURGY

The deferrination product is leached in hot (80-90°C) recycled NaCl brine, at which temperature the $PbCl_2$ solubility is high and there will be an adequate differential when it is subsequently cooled in the $PbCl_2$ crystallization step. All chlorides, including small amounts of $FeCl_2$ and $FeCl_3$, are

dissolved and the leach solution separated from the solids, which consist mainly of gangue but which under practical conditions will likely also contain a small amount of residual sulphides.

Further processing of the leach solution is as already described in connection with the low temperature chlorination process, except for the last step, which in this case is reduction of residual Fe to the ferrous state in the solution recycled to leaching.

The $FeCl_2$ solution (raffinate) from the $ZnCl_2$ solvent extraction step could be oxidized with air at 80-100°C to remove the amount of ferric hydroxide corresponding to total iron brought in with the deferrinated chlorides to the leach, according to the reaction:

$$6\ FeCl_2 + 1.5\ O_2 \rightarrow 4\ FeCl_3 + Fe_2O_3 \text{ (actually ferric hydroxide).}$$

This would leave an $FeCl_3$ solution which, if recycled without further treatment, could interfere with $PbCl_2$ and CuCl dissolution, since these chlorides form soluble complexes with $FeCl_3$. Reduction of the $FeCl_3$ is in any case required before zinc SX, and this would require additional zinc powder for reduction of Fe^{2+} in the silver recovery step, if not before. It seems preferable to reduce $FeCl_3$ in end solution with Zn powder or scrap iron to $FeCl_2$ before recycle to leaching.

The alternative is to oxidize with Cl_2 the necessary proportion of $FeCl_2$ present in the Zn SX raffinate, and remove the formed $FeCl_3$ by SX with TBP. Iron would thus be removed from the system as pure, strong $FeCl_3$ strip solution. The $FeCl_2$ + NaCl strip solution would be recycled to leaching.

PRACTICAL APPLICATION OF PROCESS

The practical application of the main process steps to a commercial plant, are commented upon below. Comments on the pyrometallurgical process application are based on excess Cl_2 stoichiometry in the chlorination step as this seems the preferred mode of operation, for reasons explained under "Review of Process".

We wish to point out that many of the design and operating assumptions described below are not proven concepts. An extensive future test program would be required to confirm or disprove these assumptions.

DRYING OF CONCENTRATE

The concentrate should be fully dried (say to <0.1% H_2O) so as to minimize the formation of HCl, which would cause corrosion problems in the gas cooling and recirculating system. A rotary or fluid bed dryer could be used for this purpose. The fluid bed alternative is preferred as the fuel is natural gas, whereas a rotary dryer would be more practical if the fuel is oil or coal. In any case, concentrate drying to a low moisture content is required for many smelting processes; equipment and operation do not therefore present any unusual problems.

PURGING OF DRIED CONCENTRATE

The dried concentrate will however contain air which is expected to react with sulphides and elemental sulphur, and thus to create a corresponding amount of SO_2 in the chlorinator. The amount of SO_2 is small but it would build up in a closed gas recycling system. In practice there will probably be a build-up of gas through the system through inleakage, requiring a small gas bleed to atmosphere (after removal of sulphur compounds such as S_2Cl_2 and SO_2). This bleed might be sufficient to control SO_2 at an acceptable level. Otherwise, it would be necessary to purge dried concentrate with N_2. This could probably be done in a small fluidized purging tank between the drier and the concentrate charge system for the chlorinator. Capital and operating costs of this purging system, if required, would be modest.

CHLORINATION

General Concept

CANMET visualized the chlorination and deferrination steps to be carried out continuously in separate compartments of a trough reactor. A conceptual design was shown in (23), p. 47, Fig. 17.

A more recent CANMET design, based on chlorination in two stages, to ensure maximum conversion of sulphides, was evolved more recently; a perspective sketch of this chlorination concept is shown in this report.

This chlorinator design consists of two reactors in series. Concentrate and most of the chlorine are charged through flash burners above the bath into the first or main chlorinator reactor. It is assumed that most of the chlorination takes place in the gas phase from burner to bath and that unreacted

sulphides remain suspended in the chloride melt.

The chloride melt with unreacted sulphides is, according to the CANMET design, transferred across an overflow weir into the much smaller adjacent finishing reactor; this transfer should however be through an underflow as the two reactors need to be separated by a wall because it is undesirable to mix the two gases, for reasons explained below. In the finishing reactor, most of the residual sulphides are chlorinated by introducing additional chlorine and nitrogen through lances discharging below the chloride melt surface. This creates turbulent conditions to achieve good contact between Cl_2 and sulphide particles. Final chloride melt is discharged at the opposite end of the finishing reactor, entraining gangue and a small amount of residual sulphides in suspension to the deferrinator.

The Ontario Research Foundation carried out a test program on the flash chlorination.[21][22]

CANMET visualize feeding say 90% of total chlorine into the main chlorinator by flash burners. These are conceived as concentric burners with dry concentrate and N_2 carrier gas blown out through the centre, while Cl_2 is supplied to an annular jacket. We understand that in tests to date the flash burner nozzle would rapidly plug up due to back reaction into the nozzle itself, or create a plug around its tip. More test work is therefore indicated before the flash burner can be considered a proven concept.

The assumption that most of the chlorination takes place in the gas phase from burner to bath, has apparently not either been demonstrated. This is an important point since unreacted sulphides will settle at the bottom of the chlorinator bath, where it can only be chlorinated by $FeCl_3$, which is however limited to about 12% of total iron chlorides in the bath, at the desired temperature (~680°C), according to (23), p. 37, Fig. 12. In the quiescent bath of the large chlorinator reactor it seems therefore probable that a significant amount of unreacted sulphides will collect in the bottom. To ensure transfer of suspended sulphides in the chloride melt to the finishing reactor, the main reactor should probably be quite small and thus avoid settling.

It has been suggested that the chlorination step might be carried out in a flash smelting unit at ∿700°C at the charge end of the reactor. The melt would be cooled naturally from volatilization of $ZnCl_2$, and discharged at the other end at say 550°C, i.e. a temperature suitable for direct transfer to the deferrination step. Chlorination temperature would not rise above 700°C as the melt would cool through increased $ZnCl_2$ volatilization. Likewise, deferrination temperature would not increase since the step is endothermic.

We have not examined this concept in detail but believe that it would present much the same problems as the previously described concept. In other words, if submerged chlorine lancing is needed to ensure complete chlorination of the sulphides, then a partition and two gas streams must be designed into the chlorinator, regardless of the type of flash burner or shape of vessel. The same applies to operational reliability of flash ignition, i.e. back reaction into the burner.

Chlorination Gases

Based on the 2-stage chlorination concept, it would be necessary to provide separate circuits for the main reactor gas and for the finishing reactor gas, as the two gases differ in composition and require different processing.

As the concentrate is flash burned with Cl_2 deficiency, the main reactor gas should be free of sulphur chlorides and therefore suitable for sulphur recovery and recycle of N_2 to the chlorination step.

The finishing reactor gas, on the other hand, will contain chlorine and sulphur chlorides since excess Cl_2 is introduced through the lances. The gas is also likely to contain chloride melt spray from the submerged lances, as well as volatilized chlorides. At least the melt spray and volatilized chlorides would have to be removed, perhaps by shock cooling with cold N_2 followed by cyclones, before the gas could be compressed for re-introduction to the chlorination flash burners and/or lances. It is difficult to imagine indirect cooling of the finishing reactor gas without creating crusts of frozen melt spray; shock cooling with nitrogen, on the other hand, increases the

circulated gas volume, making it necessary to bleed off a similar gas volume from the circuit. Consequently, recovery of Cl_2 from the finishing reactor gas creates practical problems, whereas bleed-off to atmosphere of this gas would be environmentally unacceptable so that expensive gas cleaning, with losses of sulphur and chlorine values, would be required before discharge to atmosphere.

Temperature Control

Chlorination should be maintained around 680°C; this applies to flame temperature as well as bath temperature. A higher flame temperature could result in excessive $ZnCl_2$ volatilization, while a lower bath temperature would cause zinc sulphide particles to be passivated by a frozen $ZnCl_2$ film.

The Ontario Research Foundation has calculated theoretical flame temperatures (TFT) and their results are shown in (22), p. 15, Fig. 9. This chart shows how the flame temperature is lowered and hence the extent to which the heat balance is adversely affected by:

1. excess chlorine
2. $ZnCl_2$ volatilization
3. nitrogen dilution.

The combination of 10% excess Cl_2, 7.59 Cl_2/N_2 weight ratio (= ∿3 Cl_2/N_2 volume ratio), and 10% $ZnCl_2$ volatilization already reduces the TFT to ∿580°C, i.e. an insufficient flame temperature. This leads to the following conclusions.

1. The reactor, with gas offtake, etc., must be highly insulated.
2. Incoming gases (Cl_2 and N_2) must be preheated to the highest temperature which seems feasible; nitrogen could be preheated to say 450°C. In practice, it might be more difficult to supply hot chlorine to the burner system but it should be possible.
3. Minimize nitrogen amount; this is desirable to reduce $ZnCl_2$ volatilization but a certain nitrogen-to-concentrate ratio is required to effectively blow the concentrate through the flash burner and spread it out in the reactor chamber.

Even if these requirements are met, it must be possible to heat the furnace, in order to control the temperature. Direct burning of any fuel into the furnace atmosphere would change gas composition and might bring in undesirable components such as CO_2, CO, $COCl_2$ (phosgene), HCl, CS_2, COS, etc. Any form of electric heating (resistance, electrodes or induction) does not seem practically feasible in that environment.

When it comes to maintaining temperature, the finishing reactor presents an even greater problem. Comparatively little chlorine is added here, limiting the amount of chlorine reaction when generated. Again, the question is whether there exists any practical way of providing auxiliary heat. It seems difficult to visualize feeding preheated chlorine through lances which should be replaceable and therefore retractable.

Flash burners as well as lances should probably be water-cooled, to achieve a reasonable life for this equipment. This would add to heat losses in both reactors.

We therefore believe that serious problems would need to be overcome in order to maintain a commercial scale chlorinator operation at the desired temperature.

Materials of Construction

The reactor environment is somewhat similar to that in an electrolytic magnesium cell, where a chloride melt is electrolyzed at ~780°C and where chlorine gas is evolved at the anodes. Magnesium cell lining consists of high quality refractory bricks (typical composition 75% SiO_2, 24% Al_2O_3, 2% Fe_2O_3). Bricks are very closely fitted and joined with a special cement, and the inner brick surface is glazed. Such a lining would probably be suitable for the chlorination reactors and gas offtakes.

Highly insulated, bricked flues could be used for high temperature gas ducts. Cast iron and particularly silicon iron stand up to dry chlorine up to 500-600°C, but these materials are brittle and therefore not suitable for ducts with large cross-sections. Steel ducts are used for chlorine gas in magnesium plants, at temperatures up to say 300-350°C.

The above materials stand up to chloride melts and Cl_2 containing gases in magnesium plants, but the effects of elemental sulphur and sulphur chlorides on them are probably unknown at present.

The Ontario Research Foundation used 304 stainless steel burners but these deteriorated fast without water cooling. Their large scale reactor burner design concept is therefore water-cooled.

Outokumpu's latest burner design (the "inverted mushroom burner"), for flash smelting furnaces could perhaps be adapted for this process, using a small volume of high pressure nitrogen to spread a concentrate suspension in Cl_2 over a wide area. Maybe a single flash burner of this type could be used for feeding a main reactor of similar shape as a small flash smelting furnace. It might be made of a ceramic material, cast iron or silicon iron. The main reactor could be designed like a small Outokumpu flash furnace, to ensure impingement of molten chloride drops onto the bath and thus reduce spray carry-over.

The question of a suitable material for lances in the finishing reactor might be difficult to solve. Water cooling would be needed to avoid rapid deterioration of lances made of stainless steel but this may not be feasible as the chloride melt would probably freeze onto and block the lance tips.

Graphite tubes stand up to chlorine gas, at least up to the 680-720°C range, since they are commonly used for chlorine fluxing of molten aluminum. Graphite is also likely to stand up to the chloride melt since graphite anodes are used in magnesium electrolysis. Consequently, we are inclined to think that graphite may be the best commonly available material for the lances. Graphite is however brittle and the lances should therefore be as short as possible. A finishing reactor with low headroom should be possible, to satisfy this requirement. The lances should also be replaceable during operation, and therefore retractable. This may not be an easy requirement to satisfy in a fully sealed reactor.

DEFERRINATION

In CANMET's original but later abandoned trough reactor concept (23),

p. 37, Fig. 17, the chloride melt was deferrinated on a compartment forming an integral part of the reactor.

CANMET's more recent concept is based on a reactor similar to the chlorination finishing reactor, into which $Cl_2 + N_2$ carrier gas are introduced into the melt through submerged lances to provide intimate contact between $FeCl_2$ in the melt and Cl_2 in gas. A large volume of nitrogen carrier gas is necessary to efficiently remove Fe_2Cl_6 vapour; to maintain the deferrinator at the desired temperature of ∿525°C, and to avoid freezing around the lance tips, it will probably be necessary to preheat the $N_2 + Cl_2$ mixed gas, or at least the nitrogen.

Again, the heat of reaction is probably not sufficient to compensate for radiation and Fe_2Cl_6 evaporation heat losses, but some heat is available from cooling of incoming chloride melt from dechlorination (680°C) to deferrination temperature (525°C).

Comments regarding reactor design and materials as well as lance material, also apply here.

Again, the possibility of using graphite lances is probably the most interesting. On the other hand, we believe that any kind of metallic lances would require cooling and that this could lead to freezing and blocking of lance tips. Submerged lances have been extensively tested by Mitsubishi and by CRA (in connection with the Worcra process), for continuous copper smelting and converting, without success. The Worcra process was abandoned, in part due to the problem of maintaining lances, while Mitsubishi changed over to lances discharging close to but still above the bath surface; their process has now been successfully working for years this way.

It might be possible to blow $Cl_2 + N_2$ through a lance onto the surface of a rapidly moving melt, in a TBRC (top blown rotary converter)-like vessel. The fast rotation would progressively expose a fresh $FeCl_2$ surface to the chlorine. However, this would be a batch operation which cannot be seriously considered in this context. Also, it would be practically impossible to completely seal the gas offtake of a tilting and rotating vessel.

DECHLORINATION

Assuming that the deferrination equipment and operating problems could be solved, one must now consider how to convert gaseous $FeCl_3$, diluted with nitrogen, into marketable or at least disposable Fe_2O_3 in commercial scale equipment.

If dechlorination could be carried out with both reactants ($FeCl_3$ and O_2) in the gaseous state, then theoretically the reaction would be thermally self-sustaining and therefore require no outside energy, except for producing the necessary oxygen. In order to produce an Fe_2O_3 product which is saleable or disposable to waste, the iron oxide product must be of reasonable grain size and practically free of water soluble chlorides such as $FeCl_2$, $FeCl_3$, $ZnCl_2$, etc.

Our comments are mainly based on dechlorination test reports published by the U.S. Bureau of Mines,[28] Mitsubishi[29] and Toho Titanium.[24]

Grain Size of Iron Oxide

Mitsubishi[29] operated a sizeable pilot plant for dechlorination in the gaseous phase, using two insulated cylindrical towers in series, 0.8 m Ø x 3.7 m H. $FeCl_3$ containing gas was introduced at the top of the first tower, and oxygen, in 5-10% stoichiometric excess, was injected through nozzles in its upper part. Reacted gas was transferred from the bottom of the first tower to the bottom of the second tower where it moved upwards and was discharged at the top. Total residence time was 90 seconds. Gas temperatures were as follows:

Reaction zone, 1st tower	900°C
Outlet, 1st tower	700-750°C
Outlet, 2nd tower	600°C

The produced Fe_2O_3 was extremely fine, averaging 7 microns. Practically all of it was carried out with the gas and removed in a hot cyclone followed by a wet venturi scrubber which cooled the gas to room temperature. Purified gas, containing ∿52% Cl_2 was dried countercurrently in several stages with concentrated H_2SO_4 before compression and liquefaction.

This indicates that the reaction between gaseous $FeCl_3$ and O_2 will not

produce ferric oxide with the physical characteristics required for either waste disposal or large scale use in the steel industry, keeping in mind that the pigment industry offers only a very limited market for fine iron oxide products.

A coarse ferric oxide could be produced if $FeCl_3 + O_2$ could be made to react on the surface of Fe_2O_3 granules; these could for example descend through a column and would grow in the way that nickel pellets grow when nickel carbonyl gas is decomposed in the Inco carbonyl nickel refining process. However, there is no evidence, at least to our knowledge, that this can be achieved; in the meantime we must assume that the reaction between gaseous $FeCl_3 + O_2$ will produce an extremely fine Fe_2O_3 product.

Consequently, we have based our process evaluation on the dechlorination of solid $FeCl_3$. The U.S. Bureau of Mines[28] has carried out this reaction in a laboratory scale reactor at 500-550°C, using a fluidized bed of Fe_2O_3. Optimum processing was attained with an $FeCl_3$ feed containing 25% Fe_2O_3 granules with 2% NaCl as catalyst. Conversion of $FeCl_3$ was 94-97%, and up to 92% of the stoichiometric Fe_2O_3 was removed in the primary reactor discharge, indicating that most of the product was granular but that still 8% reported as dust in the gas stream.

The most thorough and realistic pilot plant test work on fairly large scale was carried out by Toho Titanium.[24] Furthermore, Toho recirculated fines to their fluid bed chlorinator, thus converting all the iron oxide into granular form. Since Toho Titanium provides the most reliable information on industrial application of this step, we have based our dechlorination concept on the published Toho data.

Contamination with Chlorides

The fine ferric oxide produced by Mitsubishi from reacting gaseous $FeCl_3 + O_2$ contained:

	%
Fe_2O_3	95.2
$FeCl_2$	0.32
$FeCl_3$	0.23
$MnCl_2$	1.29
Balance	mostly other chlorides

We believe that this product contains too much soluble heavy metal chlorides for safe disposal or use as an iron oxide raw material.

This problem was solved by Toho Titanium who recirculated dust to the fluid bed reactor, yielding a low chloride product.

Information provided by CANMET regarding vapour pressure of $ZnCl_2$ over a mixed chloride melt indicates that a considerable proportion of $ZnCl_2$ formed in the chlorinator at 680°C will remain in the chloride bath. Furthermore, some ZnS will remain in unreacted sulphides going through to deferrination. Consequently, one must be prepared for a small amount of volatilized $ZnCl_2$ in deferrinator offgas, in spite of $ZnCl_2$ vapour pressure being quite low at deferrination temperature (525°C). Gas entrained chloride melt droplets might also be present. $ZnCl_2$ is obviously undesirable in the iron oxide product where it would be present since conversion of zinc chloride to oxide does not occur at the dechlorination temperature, unless removed prior to dechlorination. In the application of the high temperature chlorination process to zinc rich concentrates, it seems therefore prudent at this time to assume a flowsheet which will eliminate $ZnCl_2$ before dechlorination.

Conceptual Dechlorination Based on Toho Titanium Process

$ZnCl_2$ can probably be condensed selectively by cooling deferrinator gas to ∿350°C. This would require a mechanically cleaned (shot cleaning, for example) heat exchanger from which the impure solid $ZnCl_2$ could be extracted and recycled to the chloride melt going to leaching.

Based on Toho's experience, $FeCl_3$ would then be condensed at 150-170°C, yielding $FeCl_3$ powder and a gas consisting of $N_2 + Cl_2$ for chlorine recovery.

The $FeCl_3$ powder would be charged to a fluid bed dechlorinator operating at ∿700°C. Toho operated a 0.7 m Ø x 3 m H fluid bed dechlorination reactor which had a Cl_2 recovery capacity of 1.2 MT/day. Fluid bed reactor offgas would be cooled to collect Fe_2O_3 fines + $FeCl_3$ dust, which would be mixed with the $FeCl_3$ powder from the solid condenser to form the fluid bed dechlorinator feed shown on the dechlorination flowsheet. Toho explains that Fe_2O_3 formed in the dechlorinator sticks to the fluidized particles which grow and remain in the reactor, so that a granular product is discharged, containing in their case <0.1% Cl.

Nitrogen has already been removed with the solid $FeCl_3$ condenser offgas. The dechlorinator gas, containing Cl_2 and ∿20% excess oxygen, based on the oxygen efficiency in the dechlorinator step predicted by Toho for a commercial operation, is cleaned for removal of $FeCl_3$ and fine Fe_2O_3 before chlorine recovery by liquefaction.

It seems feasible to carry out this dechlorination flowsheet in generally known equipment. A brick-lined reactor is probably suitable for dechlorination, and insulated steel ducts should stand up to the gases, provided the system is kept free of HCl from moist air inleakage.

Three condensers recovering solid $ZnCl_2$ and $FeCl_3$ are required for the flowsheet. These must be of the "self-cleaning" type; perhaps shot cleaning with ceramic balls would be suitable for this purpose. These condensers might recover the heat in the form of steam, as suggested in a CANMET mechanical flowsheet.

A problem which should be mentioned, is how to handle possible splash of chloride melt carried over from the deferrinator, and which could cause problems in the deferrinator offgas system, since this area might be inaccessible to cleaning from outside during operation, due to the nature of the gas. To resolve this problem, the $ZnCl_2$ condenser should be placed close to the deferrinator gas offtake.

PROCESSING OF GASES

Based on the above description of the process based on excess Cl_2 stoichiometry in overall chlorination (but Cl_2 deficiency in the first main reactor) the following gas streams are produced:

Gas Stream	From	Temp. °C	Contains
	Chlorination:		
1	1st (main) reactor	680	N_2, S_x, $ZnCl_2$
2	2nd (finishing) reactor	680	N_2, S_2Cl_2, some excess Cl_2.
	Dechlorination:		
3	solid $FeCl_3$ condenser	<170	N_2, excess Cl_2
4	dechlorination gas cooler	<170	Cl_2, excess O_2

Chlorination gases are also likely to contain minor amounts of other volatile chlorides and elements, such as As, Cd, Hg, Fe, etc., depending on concentrate composition. The behaviour and ultimate safe disposal of these impurities would be a major research topic if this process is further developed.

SULPHUR RECOVERY FROM CHLORINATION GASES

It seems feasible to recover sulphur from Gas Stream 1 from the main reactor, but utilization of Gas Stream 2 from the finishing reactor seems more problematic.

Processing of Main Chlorination Reactor Gas

This gas consists mainly of sulphur vapour and nitrogen. It also contains some volatilized $ZnCl_2$, and probably minor amounts of other chlorides.

It has been suggested that zinc chloride should be recovered as liquid $ZnCl_2$ by cooling to 450-500°C with cold nitrogen. Such a condenser should be located immediately adjacent to the main chlorination reactor, to catch any chloride melt spray and unreacted concentrate which would be carried over with the gas. The condenser could be a brick-lined chamber or cyclone into which the cold nitrogen is admitted; impure liquid $ZnCl_2$ would be tapped from the bottom. It may be necessary to provide a spare unit for clean-out of dross from carried-over solids, without interrupting the chlorination operation. Hopefully, other chlorides will be condensed with $ZnCl_2$ but Fe_2Cl_6 is still volatilized at this temperature and will go through to sulphur condensation.

The subsequent sulphur condensation should be carried out at <150°C, the temperature at which molten sulphur has its minimum viscosity. The sulphur condenser could be visualized as a spray condenser, i.e. a chamber where the gas is cooled from 450-500 to <150°C by a shower of recirculated molten sulphur, which is cooled as a liquid in heat exchangers. A bleed stream from the sulphur condensation circuit would be solidified, for example in a prilling tower where a shower of liquid sulphur freezes by falling through an ascending stream of ambient air.

The condenser offgas will be nitrogen with low sulphur vapour content. If little nitrogen is used then this nitrogen might be discharged to atmosphere following incineration of the contained sulphur, resulting in a very limited SO_2 emission. This would avoid the problem of residual sulphur condensation in the nitrogen recycle stream.

If a substantial volume of nitrogen is needed in the first chlorination reactor, then the sulphur condenser offgas should be recycled to the chlorination reactor. It should then be reheated in a gas or steam heated heat exchanger to avoid residual sulphur condensation in the recycle ductwork.

Processing of Finishing Chlorination Reactor Gas

This gas is difficult to process for sulphur recovery because it contains sulphur chlorides and excess Cl_2, besides metal chlorides in the form of volatilized chlorides and possibly chloride melt spray. Regardless of how

this gas is ultimately treated, one must first remove $ZnCl_2$ and other chlorides and this could be done by shock cooling with nitrogen, as already described. The recovered chlorides would be transferred to the main chloride melt stream.

Ideally, the clean gas should be recycled in some way to the first (main) chlorination reactor, to utilize its chlorine content and ultimately recover its sulphur content. However, one cannot allow this gas into the first reactor chamber as sulphur chlorides and excess chlorine go directly through to the offgas and create problems downstream in sulphur condensation. Even if one could recycle this gas through the main reactor flash burners (and this is difficult to visualize) there still might be a possibility of sulphur chlorides going through to the main gas stream. It appears therefore that the finishing reactor gas, following removal of $ZnCl_2$ and other metal chlorides, might have to be scrubbed with a caustic solution (NaOH or Na_2CO_3) for removal of its S and Cl contents, before discharging the remaining nitrogen to atmosphere. Whether this is economically feasible, depends on how much unreacted sulphides remain after the first chlorination step, and how much excess Cl_2 is needed in the second chlorination step.

Chlorine Recovery from Dechlorination Gases

Gas from the solid $FeCl_3$ condenser contains only $N_2 + Cl_2$ and can therefore be recycled to deferrination after preheating to >525°C.

Gases from the dechlorination gas cooler, containing O_2 as well as N_2 besides Cl_2, goes to liquid chlorine recovery by cooling and compression. However, following solid condensation at 150-170°C, the gases probably still contain fine particles of Fe_2O_3 and possibly $FeCl_3$ which must be extensively removed before the gases are suitable for compression. This should preferably be done by filtering the gases through a bag filter, as the gases must be completely dry for compression and liquid chlorine recovery. Otherwise, it would be necessary to wet scrub the gas and dry it before chlorine liquefaction, as Mitsubishi had to do in their pilot plant; this would add considerably to the complexity and cost of chlorine recovery.

Materials of Construction

Insulated steel ducts are probably suitable for handling all these gases as long as humidity is excluded. All gas systems must therefore be completely sealed for operating at a slight negative pressure to avoid the risk of poisonous gases leaking out into the working atmosphere.

HYDROMETALLURGICAL PLANT

Preparation of Chlorides for Leaching

It has been suggested that the chloride melt, tapped from the deferrinator at 525°C, be granulated with oxygen to convert residual iron chlorides into insoluble Fe_2O_3. In practice this seems difficult to perform in any known type of equipment. Also, this operation seems hardly necessary if deferrinated chloride melt contains only 1-2% Fe (approximately equally divided between ferric and ferrous iron). It would be simpler and probably adequate to granulate the chloride melt in a prilling tower. In this, the melt would be distributed on a revolving disc and the resulting shower of chloride drops would be solidified in an ascending stream of cold air.

Theoretically it would have been attractive to utilize the heat content of the molten chlorides by pouring them directly into recycled NaCl brine. This would require a large recycle and cooling in external heat exchangers of the solution. It is unlikely to be a practical and economic alternative.

Leaching

Granulated chlorides would be leached concurrently in recycled NaCl brine in a series of agitated tanks.

Liquid/Solids Separation

There is likely to be only a small amount of solids (gangue and residual sulphur corresponding to 0.5-1% S in deferrinated chlorides). Direct filtering of the slurry without thickening should therefore be sufficient. Automatic chamber filters would be a suitable design.

Lead Chloride Crystallization

Vacuum cooling crystallizers are suitable to ~40°C. If it is desirable to remove more $PbCl_2$ and if cold cooling water is available, then additional crystallization could be achieved by further cooling in contact cooling crystallizers. $PbCl_2$ crystals can be filtered and countercurrently washed on horizontal belt filters. The crystals must then be completely dried in shelf or belt dryers. The drying system must be well enclosed and vented since $PbCl_2$

vapour pressure is significant at the drying end temperature.

Electrolytic Lead Recovery

Dried $PbCl_2$ crystals are transferred and charged to electrolytic cells in an enclosed system (drag conveyors, for example). Lead electrolysis is carried out at ∿450°C in an electrolyte consisting of $PbCl_2$ dissolved in a mixture of alkali chlorides. LiCl is beneficial as it improves conductivity and reduces $PbCl_2$ vapour pressure, but lithium salts are expensive and the use of LiCl therefore requires strict housekeeping and reprocessing of any electrolyte bleed found necessary for impurity control.

Several fused salt electrolytic lead cells have been tested on pilot plant scale. The U.S. Bureau of Mines and Hazen Research have tested unipolar cells with graphite anodes projecting from above into the bath, while lead is collected from the cathodic bottom of the cell. Due to low productivity, a large number of cells and corresponding floor area are required with this cell type.

Alcoa (Aluminum Company of America) has developed a bipolar cell for aluminum electrolysis from $AlCl_3$ in a chloride electrolyte. This cell design consists of horizontally stacked graphite electrodes, resulting in high production capacity per cell. The cell is water jacketed for accurate temperature control. Alcoa tested a prototype cell on $PbCl_2$, with good results. The Alcoa bipolar cell would probably therefore be a good selection for this operation.

Due to its solubility, impurities cannot in practice be completely washed out of $PbCl_2$ crystals. Lead bullion tapped from the cells is therefore likely to contain minor impurities which could be removed from the liquid bullion by known methods, before casting the refined lead.

Anodic chlorine gas is dry but is likely to be diluted by some air inleakage. In that case it will have to be sent to the gas separation plant to recover pure chlorine for recycle to chlorination. With completely sealed Alcoa cells, it should be possible to recycle the anode gas directly to chlorination.

Copper Removal and Recovery

The reagent DS5443 recently developed by ICI and tested in Elkem's chloride process pilot plant, permits extraction of copper from a chloride solution by solvent extraction. This reagent is highly selective only for copper in the cupric form and could be applied directly to the leach solution, based on the assumption that copper will be present in deferrinated chlorides in the form of $CuCl_2$. If copper should be present as CuCl, however, then it would be necessary to convert this to $CuCl_2$ by limited Cl_2 sparging into the solution before the copper SX step. This would however at the same time probably convert all iron to the ferric stage, which is undesirable for the subsequent silver recovery and zinc SX steps.

SX strip solution would be a relatively pure $CuCl_2$ solution from which copper would be electrowon in cells equipped with diaphragms. Wet Cl_2 gas is evolved from the anode compartments and would have to be dried before liquefaction by cooling and compression, and subsequent recycle to chlorination.

Copper could possibly be deposited as solid copper cathodes at low current density; cell design would be similar to that used commercially in nickel electrowinning from chloride solution. Another approach would be to operate at higher current density, using a different cell design where the copper is deposited as crystals collecting on the cell bottom. A problem in copper electrowinning from chloride solutions is the possibility of precipitating insoluble cuprous chloride at the cathode and thus contaminating the copper.

Copper powder has been produced from copper chloride solutions in a large pilot cell. We understand that solid copper cathodes have been produced in laboratory cells but we do not have specific information regarding conditions.

It is also possible to recover copper by electrolysis of a cuprous chloride solution, in a diaphragm cell where cupric and ferric (if iron is present) chlorides are formed at the anode. This approach could be applied directly to the deleaded leach solution but silver would then be deposited with the copper, while chlorine gas would not be available from copper electrowinning.

In the case of concentrates with low Cu content, copper recovery could be simplified by cementing it together with silver in the step described below.

Silver Removal and Recovery

The raffinate from copper SX is treated with zinc powder to cement silver, which is removed with excess Zn as a filter cake for shipment to a silver refinery.

At the same time, Zn powder is also consumed to reduce the $FeCl_3$ present in the leach chlorides, to $FeCl_2$.

Zinc Removal and Recovery

Zinc is removed from the solution by solvent extraction with TPB which is selective with respect to ferrous iron. $FeCl_3$ would be transferred with $ZnCl_2$ but there should be little ferric iron left after the Zn powder treatment for silver removal.

Consequently, the SX strip solution will be a comparatively pure $ZnCl_2$ solution. Small amounts of ferric iron and other impurities will nevertheless be transferred and the strip solution therefore requires purification before zinc recovery by electrowinning. The purification steps will include residual iron removal and Zn powder treatment to remove other trace impurities such as Cu, As, Pb, etc. The purified $ZnCl_2$ solution will be electrolyzed in diaphragm cells similar to those commercially used for nickel electrowinning from chloride solutions. Good quality zinc cathodes have been produced from chloride solutions in Elkem's pilot plant.

Wet anode chlorine gas must be dried before liquefaction and recycle to chlorination, as already explained in connection with copper electrowinning.

Iron Control

It is necessary to remove from the circuit an amount of iron corresponding to that introduced with the chloride feed. This can be done by oxidation of a corresponding proportion of ferrous iron in the raffinate from zinc SX, according to the reaction:

$$6\ FeCl_6 + 1.5\ O_2 \rightarrow Fe_2O_3 + 4\ FeCl_3$$

This reaction is promoted by using oxygen rather than air, and by increasing the temperature, which also improves filterability of the iron hydroxide. The

temperature should be raised to at least 80-90°C prior to the oxidation step. A more rapid reaction and a better ferric hydroxide precipitate is obtained at say 100-110°C, requiring a low pressure autoclave.

It is assumed that the ferric hydroxide can be disposed to waste. Otherwise it would have to be calcined or agglomerated at some cost.

Another possibility is to chlorinate the required amount of $FeCl_2$ by sparging Cl_2 gas into the zinc SX raffinate and subsequently remove the ferric iron by solvent extraction with TBP or TIOA. The ferric iron can be stripped as a strong $FeCl_3$ solution suitable for shipment in rubber lined tank cars and sale to water purification and sewage plants, as done by Société Le Nickel at the Sandouville nickel refinery in France.

Impurity Control

The solution from the iron control step is recycled to leaching. Accumulation of minor impurities is controlled by removing a bleed stream of the recycled solution. This bleed stream will undoubtedly have to be treated for removal of objectionable impurities such as arsenic, antimony, etc. as well as residual amounts of heavy metals, in particular lead since the recycled solution will still contain a significant $PbCl_2$ level. These impurities are probably best removed as sulphides by precipitation from the bleed stream with H_2S or Na_2S.

At the same time, NaCl will be removed with the bleed stream and will have to be replaced to maintain the desired level in the main solution circuit.

If feasible, it would be preferable to remove minor impurities after which the purified $PbCl_2$-$FeCl_2$-NaCl solution could be re-joined with the main solution stream to leaching.

Materials of Construction

The described hydrometallurgical process can probably be carried out in equipment of established design, using construction materials known to stand up under similar conditions of temperature and chloride solutions. Commercial nickel and cobalt refineries have for many years operated under similar conditions.

The following construction materials seem reasonably well established for the relevant conditions:

- tanks, including leach reactors operating at above 80°C: rubber and acid brick lined mild steel
- tanks operating below 80°C: fiberglass reinforced polyester
- autoclaves, if required, for iron precipitation: lead and acid brick lined mild steel
- agitators: titanium
- heat exchangers: titanium or possibly graphite for some applications
- filters: polypropylene, fiberglass reinforced polyester, or rubber lined mild steel, depending on type
- crystallizers: rubber lined steel
- pumps: titanium, ceramic or rubber lined, depending on application
- piping: polypropylene, backed by fiberglass reinforced polyester where temperature above polypropylene softening point
- anodes (Cu and Zn electrowinning cells): ruthenium oxide plated titanium (DSA).

Some equipment might require lining with expensive plastics such as Kynar or Reflon.

From this it is understood that reasonably well proven materials are available for the conditions encountered in this hydrometallurgical process. Many of these materials are expensive however, and this will be reflected in relatively high capital and maintenance costs. In these respects, the plant will be somewhat similar to those proposed by Elkem, Minemet and others for the direct processing of complex sulphide concentrates.

APPLICATION TO GOLD BEARING PYRITES

It has been suggested that the process might be applicable to ores or concentrates with a significant content of gold locked in with pyrite. In hydrometallurgical chloride processes, this gold is lost in insoluble pyrite tailings, unless these are treated by cyanidation, possibly requiring prior roasting.

High temperature chlorination will process the pyrite to elemental sulphur and iron oxide, and the gold should therefore be liberated. It could occur in the hot chloride melt as metallic gold particles, since gold chlorides dissociate at much lower temperatures (see Application of Dry Chlorination to Nickel-Copper Sulphide Ores). To recover this gold from the chloride leach residue, two alternatives are indicated:

1. by cyanidation of the leach residue;
2. by re-leaching the residue with chlorine at high Redox potential, to solubilize Au as chloride and subsequently precipitate it.

We wish to emphasize that we have not seen any data on the behaviour of pyritic gold in the high temperature chlorination process. The above comments are therefore purely conjectural at this time.

MATERIALS TESTED

All the CANMET and Ontario Research Foundation tests were carried out on high Zn-FeS_2 bulk concentrates from New Brunswick complex sulphide ores; in most reports the source was identified as Brunswick Mining and Smelting Limited (BM&S). Concentrates used were very similar in composition:

%	BM&S tailings concentrate	Bulk concentrate prepared by CANMET
Zn	30.2	29.9 - 30.2
Cu	0.7	0.65 - 0.7
Pb	4.0	9.5 - 10.1
Fe	22.0	19.9 - 20.5
S	38.5	36.6 - 37.3

The only significant variation is in lead content, which was ~4% in BM&S tailings concentrate, while bulk concentrate prepared by CANMET from BM&S ore contained 9.5-10.1% Pb.

ASSUMPTIONS FOR MATERIALS BALANCE CALCULATIONS

CONCENTRATE

The following concentrate analysis is assumed (approximate average of Brunswick Mining and Smelting bulk concentrates tested by CANMET, ORF, etc.).

	%
Zn	30
Cu	0.7
Pb	10
Fe	20
S	37
Others	2.3
Total	100.0

Others include oxygen, gangue, and minor impurities including silver.

CHLORINATION

Excess Chlorine

Corresponds to 1.08 Cl_2 stoichiometry, as defined by CANMET.

Conversion to Chlorides

	% of Metal in Concentrate
Zn	97
Pb	99
Cu	95
Fe	98

$FeCl_2/FeCl_3$ Ratio in Bath

7.3 at 680°C.

Volatilized Chlorides

$ZnCl_2$: 10% of total $ZnCl_2$ formed

$FeCl_3$: 2% of total Fe.

Actual Excess Chlorine

On this basis, 1.08 CANMET Cl_2 stoichiometry corresponds to 8.08% actual excess Cl_2 when considering:

1. unreacted sulphides
2. $FeCl_3$ formation.

Consequently, these two opposite factors practically cancel each other out when these assumptions are used for the calculations.

Chlorination Stages

Chlorination is divided in two stages (2 reactors in series). Chlorine addition is divided as follows:

to Stage 1 - 90% of total
to Stage 2 - 10% of total.

Stage 1 Reactor Gas

Following condensation and removal of $ZnCl_2$, $FeCl_3$ vapour carries on to sulphur condensation.

Stage 2 Reactor Gas

Excess Cl_2 here reacts with unreacted sulphides to form S_2Cl_2. Assumption distribution of excess chlorine in offgas:

½ as S_2Cl_2
½ as excess Cl_2.

Stage 2 chlorination gas will also contain some volatilized $ZnCl_2$ and $FeCl_3$. Quantities are likely to be small because of the small gas volume (no N_2 dilution required). Consequently, $ZnCl_2$ and $FeCl_3$ reporting in this gas stream have been ignored in the materials balance. In practice, this gas mix (S_2Cl_2 + Cl_2 + $ZnCl_2$ + $FeCl_3$) is difficult to process and recycle. Maybe $ZnCl_2$ + $FeCl_3$ could be condensed out at ~150°C (above S_2Cl_2 boiling point at 138°C) giving a cleaned S_2Cl_2 + Cl_2 gas which would have to be recycled to the Stage 1 reactor, presumably into the bath since the Reactor 1 atmosphere should not be

contaminated with S_2Cl_2. Otherwise, the Stage 2 reactor gas would have to be scrubbed, probably with alkali or lime, resulting in a loss of the sulphur and chlorine in this gas.

Nitrogen Dilution

Nitrogen volumes cannot be calculated as only pilot tests can provide adequate answers. In the meantime, the following assumptions have been made:

Stage 1: 30% of chlorine gas volume required to spread out concentrate in an Outokumpu type flash burner.

Stage 2: 5 x chlorine gas volume required for lances to achieve adequate turbulence in reactor bath.

DEFERRINATION

Residual Sulphides

It is assumed that all sulphides which will react have already been converted to chlorides in the chlorination. Consequently, it is assumed that no sulphides react in the deferrination step and that there is therefore no S_2Cl_2 in the deferrinator offgas.

Actually, however, small amounts of residual sulphides would probably react with excess chloride and high $FeCl_3$ in the deferrinator bath, and thus produce a little S_2Cl_2. This S_2Cl_2 would report, together with N_2 and excess Cl_2, in the offgas from the solid $FeCl_3$ condenser, which goes to Cl_2 recovery where S_2Cl_2 is likely to cause problems.

Ferric Chloride Formation

All Fe chlorides are converted to $FeCl_3$, except 1-2% Fe present as $FeCl_2$ + $FeCl_3$ in deferrinated chloride melt, of which one-half as $FeCl_2$ and one-half as $FeCl_3$, according to information obtained during meeting with CANMET in Ottawa on June 20, 1985. The $FeCl_3$ formation diagram indicates that the $FeCl_2$:$FeCl_3$ equilibrium ratio in the chloride bath at 525°C would be ∿4.4 but it seems reasonable to assume that there will be more residual $FeCl_3$ under

actual operating conditions, as one cannot expect excess $FeCl_3$ to be swept out quantitatively.

Copper Chloride

In the chlorination step, where excess reactive sulphides are still present, copper is assumed present as CuCl (Cu_2Cl_2) in the chloride melt to deferrination.

It is assumed that the large excess of chlorine will convert all CuCl to $CuCl_2$ in the deferrination step (this is important for the hydrometallurgical process).

Chlorine Addition

2 x amount required for converting $FeCl_2$ in chloride melt from chlorinator, to $FeCl_3$.

Nitrogen Dilution

The curve showing $FeCl_3$ vapour pressure over chloride melt indicates ~0.35 atm. at 525°C, corresponding to a theoretical minimum volume ratio of 1.89 N_2:1 $FeCl_3$ (ignoring excess Cl_2 gas). A much higher ratio is likely to be needed to achieve the efficient sweeping effect required to reduce the Fe content of the melt to a low level within a reasonable retention time, which can only be determined by continuous pilot scale tests. In the meantime, it is assumed that a 5 N_2:1 $FeCl_3$ (volatilized) will be required, corresponding to 0.863 N_2 : 1 $FeCl_3$ by weight.

For this calculation purpose, ferric chloride is assumed to be $FeCl_3$ (i.e. not Fe_2Cl_6).

DECHLORINATION

Oxygen

20% in excess of O_2 required for conversion of Fe_2Cl_6 to Fe_2O_3.

HIGH TEMPERATURE CHLORINATION PROCESS

MATERIALS BALANCE - PYROMETALLURGY
(units per 100 units concentrate)

	Zn	Pb	Cu^{1+}	Cu^{2+}	Fe^{2+}	Fe^{3+}	Cl	S	Others	Total
CHLORINATION										
In:										
Concentrate	30.0	10.0	0.7		20.0		-	37.0	2.3	100.0
Chlorine							66.7			66.7
										166.7
Out:										
Chloride melt	26.2	9.9	0.665	-	16.9	2.3	57.8	-	-	113.76
Solids with melt	0.9	0.1	0.035		0.4		-	0.92	2.3	4.66
Stage 1 gas	2.9	-	-	-	-	0.4	3.9	33.83	-	41.03
Stage 2 gas	-	-	-	-	-	-	5.0	2.25	-	7.25
	30.0	10.0	0.7		20.0		66.7	37.0	2.3	166.7
DEFERRINATION										
In:										
Recycled $ZnCl_2$	2.9	-	-	-	-	-	3.1	-	-	6.0
Chloride melt	26.2	9.9	0.665	-	16.9	2.3	57.8	-	-	113.76
Solids with melt	0.9	0.1	0.035		0.4		-	0.92	2.3	4.66
Chlorine	-	-	-	-	-	-	22.0	-	-	22.0
	30.0	10.0	0.7		19.6		82.9	0.92	2.3	146.42
Out:										
Chloride melt	29.1	9.9	-	0.665	0.67	0.67	37.8	-	-	78.80
Solids with melt	0.9	0.1	0.035		0.4		-	0.92	2.3	4.66
Deferrinator gas	-	-	-	-	-	17.86	45.1	-	-	62.96
	30.0	10.0	0.7		19.6		82.9	0.92	2.3	146.42

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HIGH TEMPERATURE CHLORINATION PROCESS

DISTRIBUTION OF METALS, SULPHUR AND CHLORINE

METALS DISTRIBUTION

In	Zn	Pb	Cu	Fe
Concentrate	100.0	100.0	100.0	100.0
Chloride melt to leach	97.0	99.0	95.0	6.7
Residual sulphides	3.0	1.0	5.0	2.0
In chlorinator gas	9.7*	-	-	2.0
In deferrinator gas to Fe_2O_3	-	-	-	89.3

* recycled

SULPHUR DISTRIBUTION	%	Units per 100 conc. units
In concentrate	100.0	37
Recoverable from Stage 1 chlorination gas	91.4	33.83
Losses:		
in Stage 2 chlorination gas	6.1	2.25
in unreacted sulphides	2.5	0.92
	8.6	3.17

CHLORINE BALANCE SUMMARY	Units per 100 conc. units
In:	
to chlorination	66.7
to deferrination	22.0
	88.7
Theoretically Recoverable:	
from deferrination (total)	45.1
from hydrometallurgy	35.7
	80.8
Losses (make-up chlorine required):	
from Stage 1 chlorination gas (as $FeCl_3$)	0.8
from Stage 2 chlorination gas (as S_2Cl_2 and excess Cl_2)	5.0
hydrometallurgy (Fe control): 38.2 - 35.7 =	2.1
	7.9

HIGH TEMPERATURE CHLORINATION PROCESS

CHLORINE BALANCE DETAILS
(units per 100 units concentrate)

CHLORINATION	Metals	Cl	Chlorides
In: concentrate	60.7	-	-
chlorine	-	66.7	-
Out:			
Volatilized Chlorides			
$ZnCl_2$ (10% of $ZnCl_2$)	2.91	3.154	6.064
$FeCl_3$ (2% of total Fe)	0.400	0.760	1.160
		3.914	7.224
Chloride Melt			
$ZnCl_2$	26.19	28.390	54.580
$FeCl_2$ + $FeCl_3$	19.20	25.622	44.822
CuCl	0.665	0.370	1.035
$PbCl_2$	9.9	3.386	13.286
		57.768	113.723
Stage 2 Gas (S_2Cl_2 + excess Cl_2)		5.018	
	Total	66.7	
DEFERRINATION			
In: Chloride melt		57.768	113.723
Chlorine		22.0	-
add: recycled $ZnCl_2$	2.91	3.154	6.064
		82.922	119.787
Out:			
Chloride melt, incl. recycled $ZnCl_2$			
$ZnCl_2$	29.1	31.544	60.644
$FeCl_2$ + $FeCl_3$	1.34	2.127	3.467
$CuCl_2$	0.665	0.741	1.406
$PbCl_2$	9.9	3.386	13.286
		37.798	78.803
Recoverable from hydrometallurgy: all except in iron chlorides:		35.671	
Deferrinator Gas			
$FeCl_3$	17.86	34.006	51.866
Excess Cl_2		11.118	
		45.154	
	Total	82.922	

HIGH TEMPERATURE CHLORINATION PROCESS

MATERIALS BALANCE

OXYGEN AND NITROGEN BALANCE

(Chlorine also shown)

	Weight units per 100 conc. units		
	Chlorine (Cl_2)	Oxygen (O_2)	Nitrogen (N_2)
In:			
to chlorination Stage 1	60.0	-	7.1
to chlorination Stage 2	6.7	-	13.0
to deferrination	22.0	-	44.8
to dechlorination	-	4.6	-
	88.7	4.6	64.9
Theoretically Recoverable			
from chlorination Stage 1 gas	-	-	7.1
from solid $FeCl_3$ condenser gas	11.1	-	-
from dechlorination gas	34.0	-	-
Total from gas separation	45.1		
from hydrometallurgy (Pb, Cu and Zn electrowinning)	35.7	-	-
	80.8	0.8	7.1
Losses (i.e. net make-up requirements)			
in chlorination Stage 1 gas	0.8	-	(7.1 recycled)
in chlorination Stage 2 gas	5.0	-	13.0
in iron oxide from dechlorinator	-	3.8	-
in hydrometallurgy (Fe control)	2.1	-	-
from gas separation	-	0.8*	44.8*
	7.9	4.6	57.8

* Will contain traces of Cl_2 and therefore not suitable for recycle to air separation plant. Oxygen and nitrogen make-up requirements indicate that nitrogen capacity is likely to determine the air separation plant capacity. It should produce nitrogen with very low oxygen content (as for ammonia synthesis, for example) while oxygen purity is not so important, i.e. the opposite of a conventional oxygen plant.

HIGH TEMPERATURE CHLORINATION PROCESS

MATERIALS BALANCE

PRODUCT TO HYDROMETALLURGY (from deferrination, incl. recycled $ZnCl_2$)

Per 100 conc. units

	Chloride Melt	Solids	Total
Zn	29.1	0.9	30
Pb	9.9	0.1	10
Cu	0.665	0.035	0.7
Fe	1.34	0.4	1.74
Cl	37.798	-	37.798
S	-	0.922	0.922
Others	-	2.3	2.3
	78.803	4.657	83.46

Analysis, %

	Soluble	Insoluble	Total
Zn	34.96	1.08	36.04
Pb	11.89	0.12	12.01
Cu	0.80	0.04	0.84
Fe	1.61	0.48	2.09
Cl	45.40	-	45.40
S	-	1.11	1.11
Others	-	2.76	2.76
	94.66	5.59	100.25

HIGH TEMPERATURE CHLORINATION PROCESS

FUTURE TEST WORK PROGRAM

We do not believe this process to be potentially attractive. In the event that CANMET should come to another conclusion we would suggest that the future test work should be directed towards the following objectives.

1. Continue flash chlorination tests, using Cl_2 deficiency to test the 1st stage of the 2-stage chlorination concept. Offgas should be analyzed for $ZnCl_2$, $FeCl_3$ and possible presence of S_2Cl_2. Reaction product should be collected for use in 2nd stage chlorination tests.
2. Test 2nd stage chlorination with excess Cl_2 injected into the melt. Analyze offgas for S_2Cl_2. Collect fully chlorinated melt for deferrination tests. It is important to determine the cut-off point between 2nd stage chlorination and deferrination; it is desirable to complete the chlorination with minimum excess Cl_2 so as to minimize premature deferrination effect in this step.
3. Deferrinate item 2 product by Cl_2 injection, and determine $FeCl_3$ volatilization vs temperature and N_2/Cl_2 ratio. Determine residual Fe vs time, and Fe^{3+}/Fe^{2+} ratio in residual Fe. Try to condense, collect and analyze $FeCl_3$ from the offgas.

Further tests would probably have to be on a larger pilot scale and cannot be planned before the above subjects have been reasonably well investigated.

HIGH TEMPERATURE CHLORINATION PROCESS

SOURCES OF INFORMATION

18. H.W. Parsons and J.B. Kearns: "The Dry Chlorination of Zn/Pb/Cu Sulphide Ores: 4. Effect of Dilution with Nitrogen at Temperatures up to 500°C, December 1977, CANMET Report MRP/MSL 77-383(IR).

19. P. Pint and W.J.S. Craigen: "Application of Chloride Pyrometallurgy to the Extraction of Base Metals from Sulphide Concentrates", October 1981.

20. F.J. Kelly: "Preliminary Economic Evaluation of the Dry Way Chlorination-Oxidation Process on Zn-Pb-Cu Sulphide Bulk Concentrates", April 1978, CANMET Report MRP/MSL 78-95(TR).

21. W.F. Fossen, "Flash Chlorination of Zinc-Lead-Copper Sulphide Bulk Concentrate, Progress Report No. 4, Final Report of Preliminary Burner Trials", June 1980, ORF Contract No. 72025.

22. H.G. Brandstatter et al: "Flash Chlorination of Zinc-Lead-Copper Sulphide Bulk Concentrate" - Summary Report, March 1981, ORF Contract No. 72025.

23. P. Pint and V.M. McNamara: "Chlorination of Zn-Pb-Cu-Ag-Fe Sulphide Concentrates Employing Submerged-Lance Chlorine Injection", May 1982, CANMET Report MRP/MSL 82-76(IR).

24. M. Ogawa et al: "A Study of Titanium Resources and its Chlorination Process", Titanium 1980, AIME publication, pp 1937-1945.

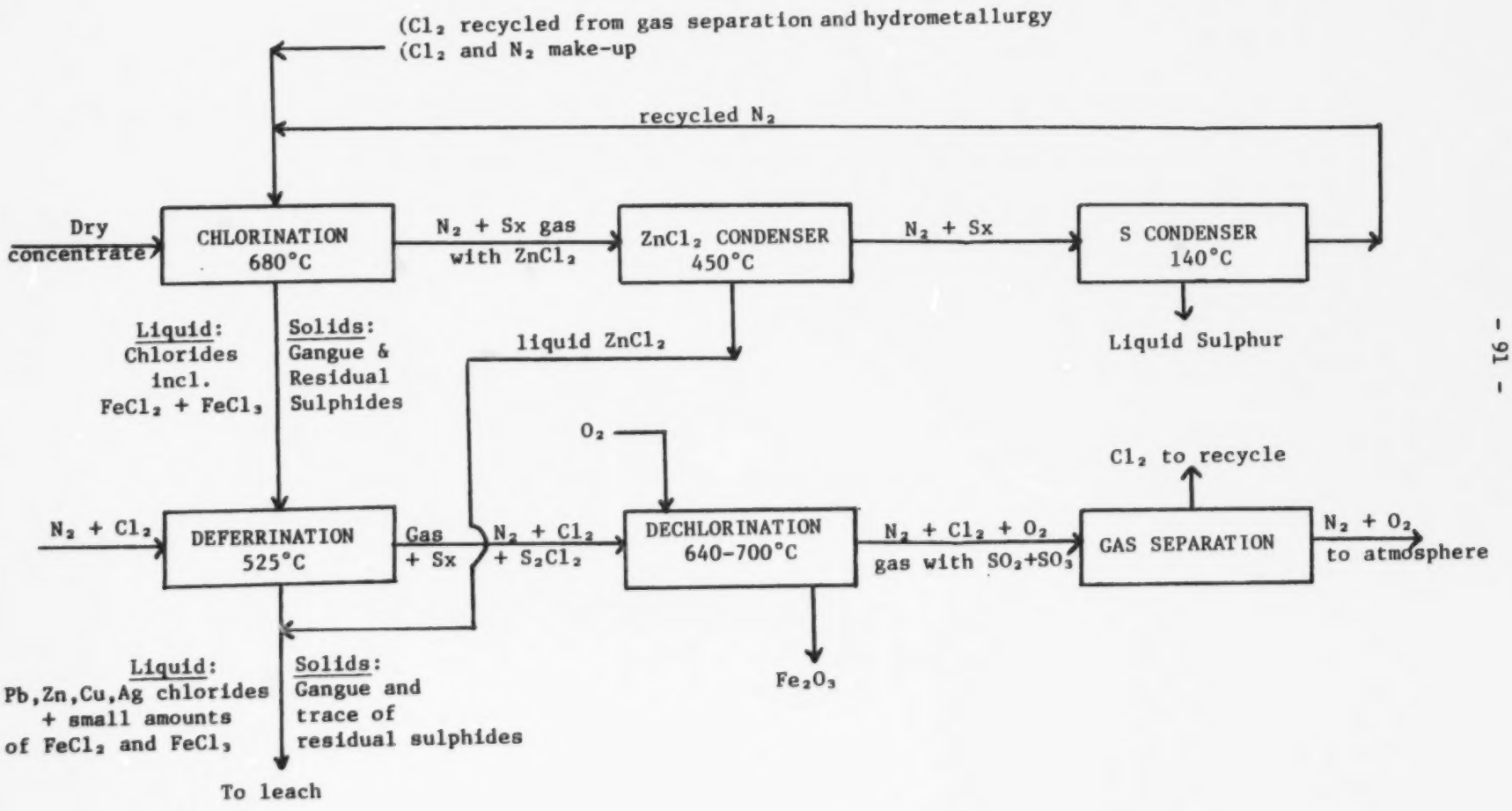
28. H.M. Harris et al: "Process for Chlorination of Titanium Bearing Materials and for Dechlorination of Iron Chloride", World Mining and Metals Technology, Joint MMIJ-AIME Proceedings, pp 693-712.

29. S. Fukushima and Y. Sugawara: "Mitsubishi Process for Upgrading Ilmenite and Chlorine Recirculation", AIME 1974 Light Metals, pp 443-466.

HIGH TEMPERATURE CHLORINATION PROCESS

Flowsheet 1: Pyrometallurgical Circuit

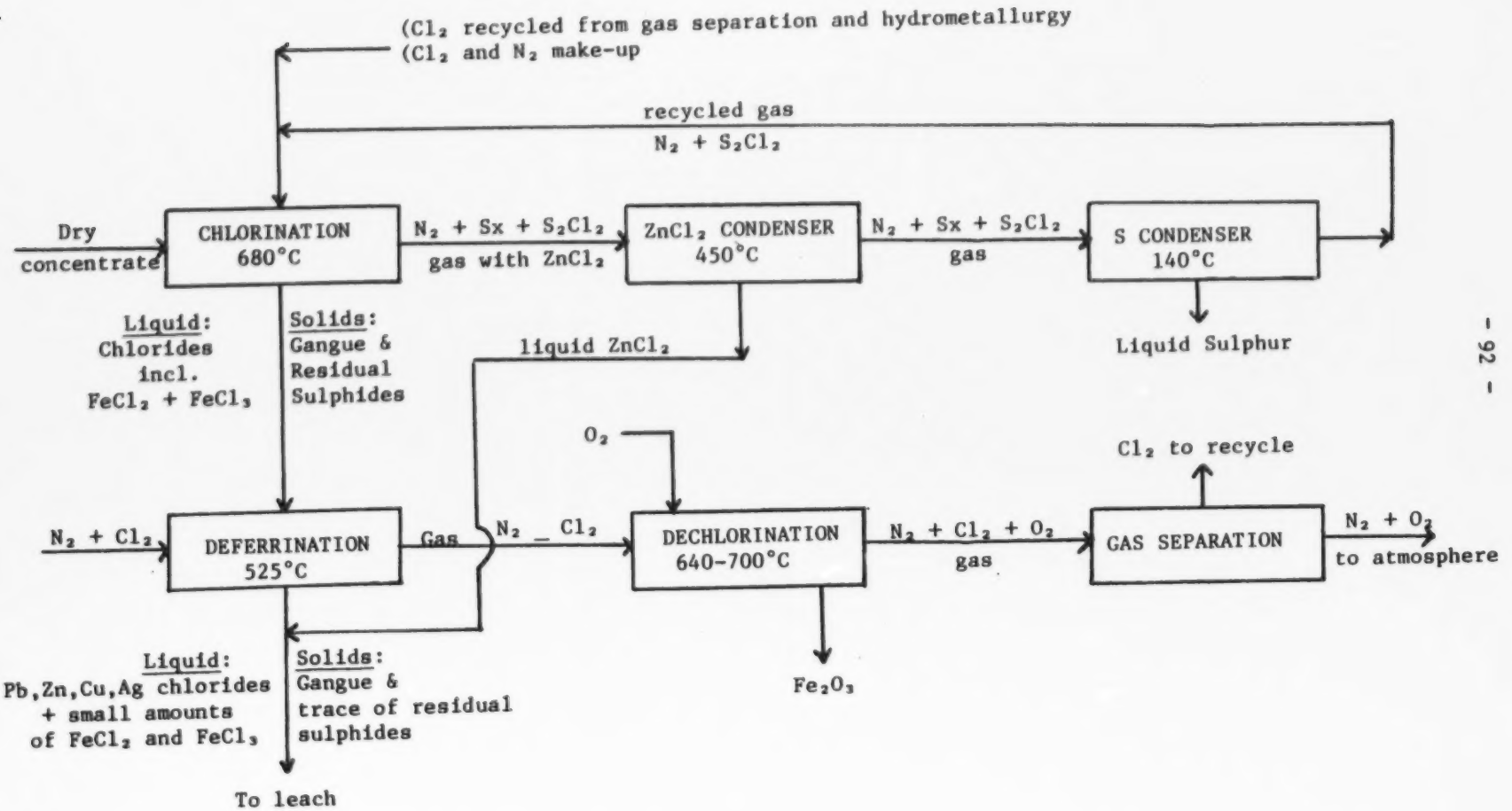
with stoichiometric deficiency of Cl_2 to chlorination



HIGH TEMPERATURE CHLORINATION PROCESS

Flowsheet 2A: Pyrometallurgical Circuit

with stoichiometric excess of Cl_2 to chlorination
(see Flowsheet 2B for two-stage chlorination)



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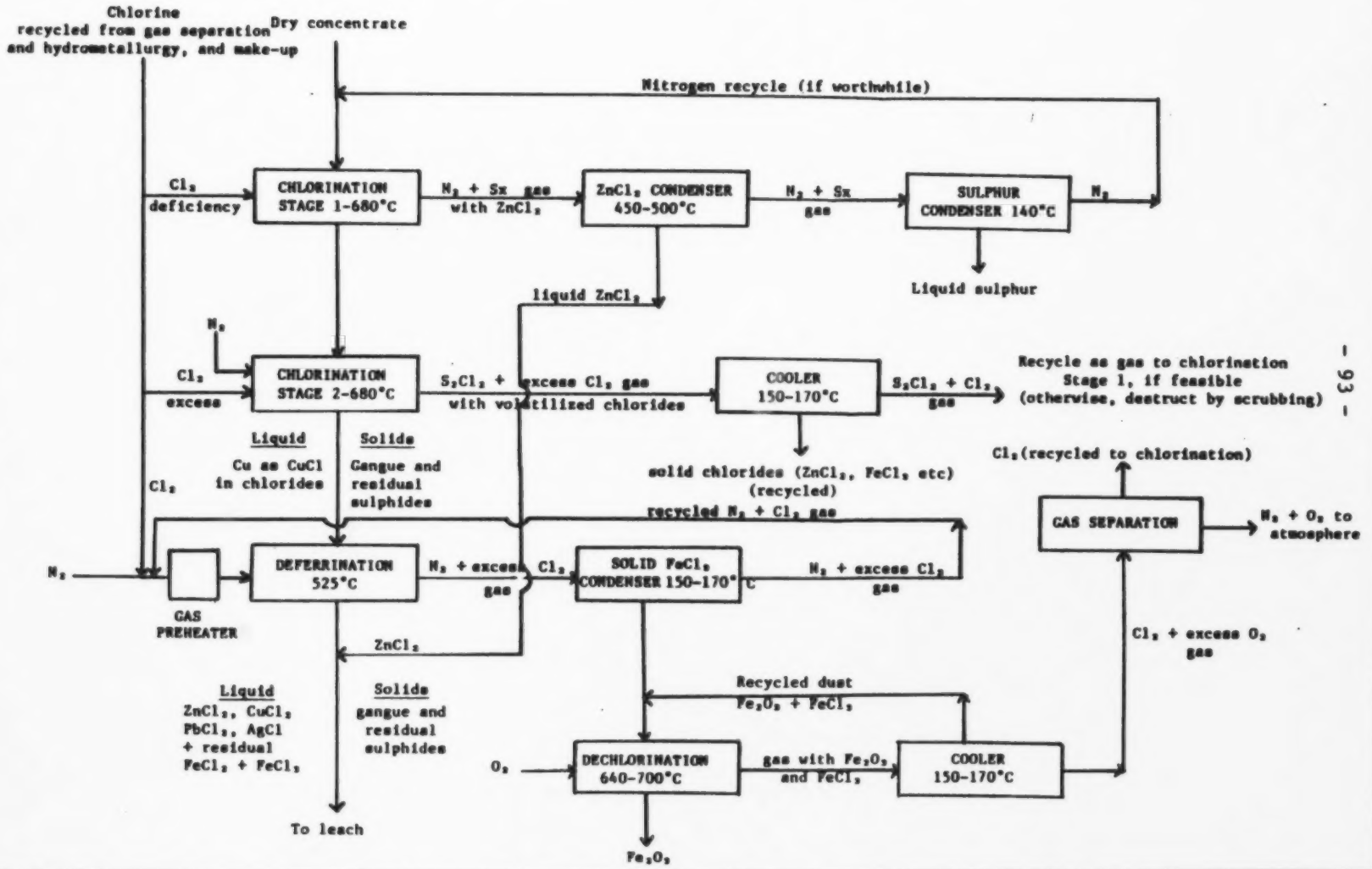
HIGH TEMPERATURE CHLORINATION PROCESS

Flowsheet 2B: Pyrometallurgical Circuit
with stoichiometric excess of Cl_2 to chlorination
Two-stage chlorination with chlorine deficiency in 1st stage
and excess chlorine to 2nd stage.

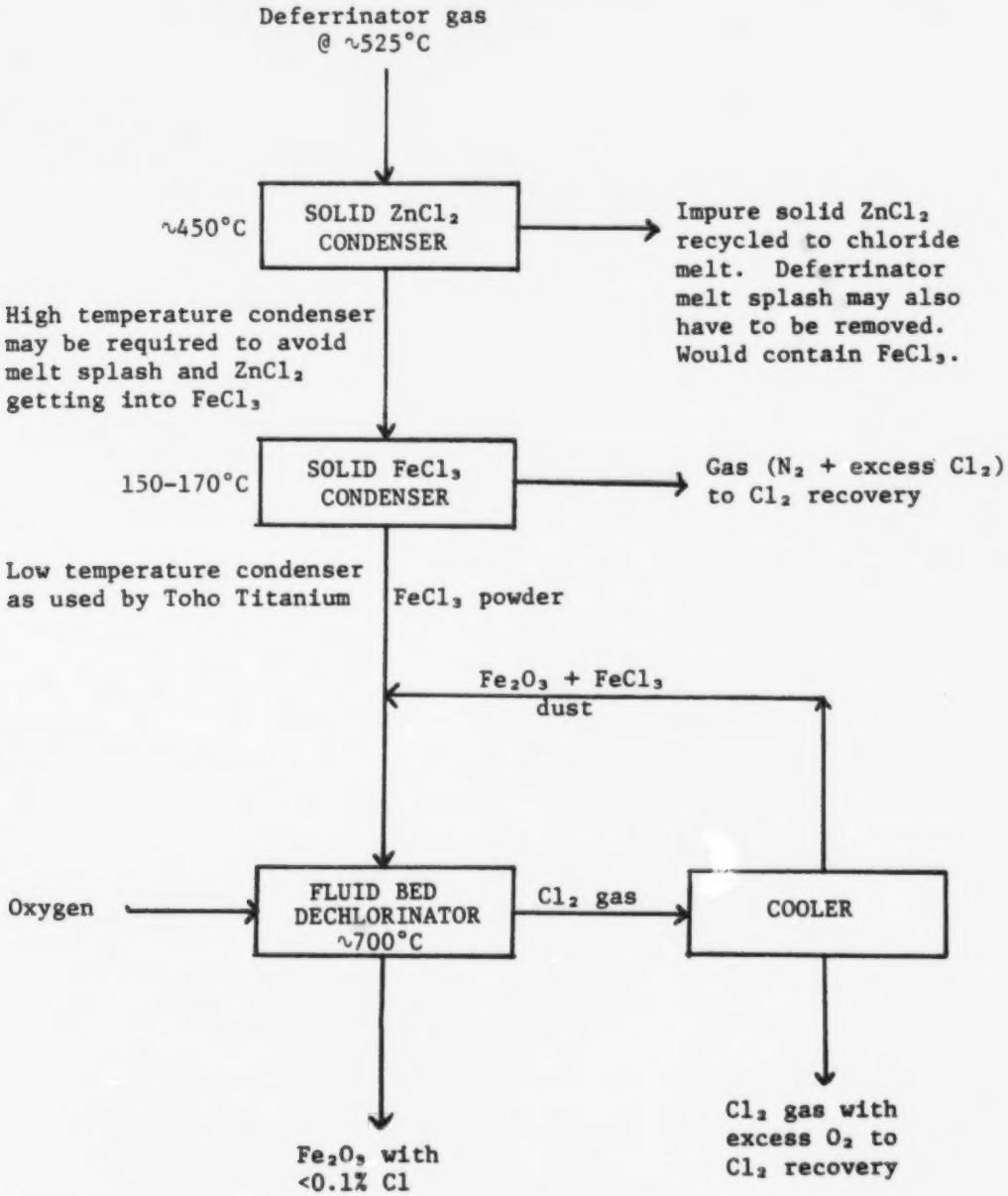


HIGH TEMPERATURE CHLORINATION PROCESS

Flowsheet 3

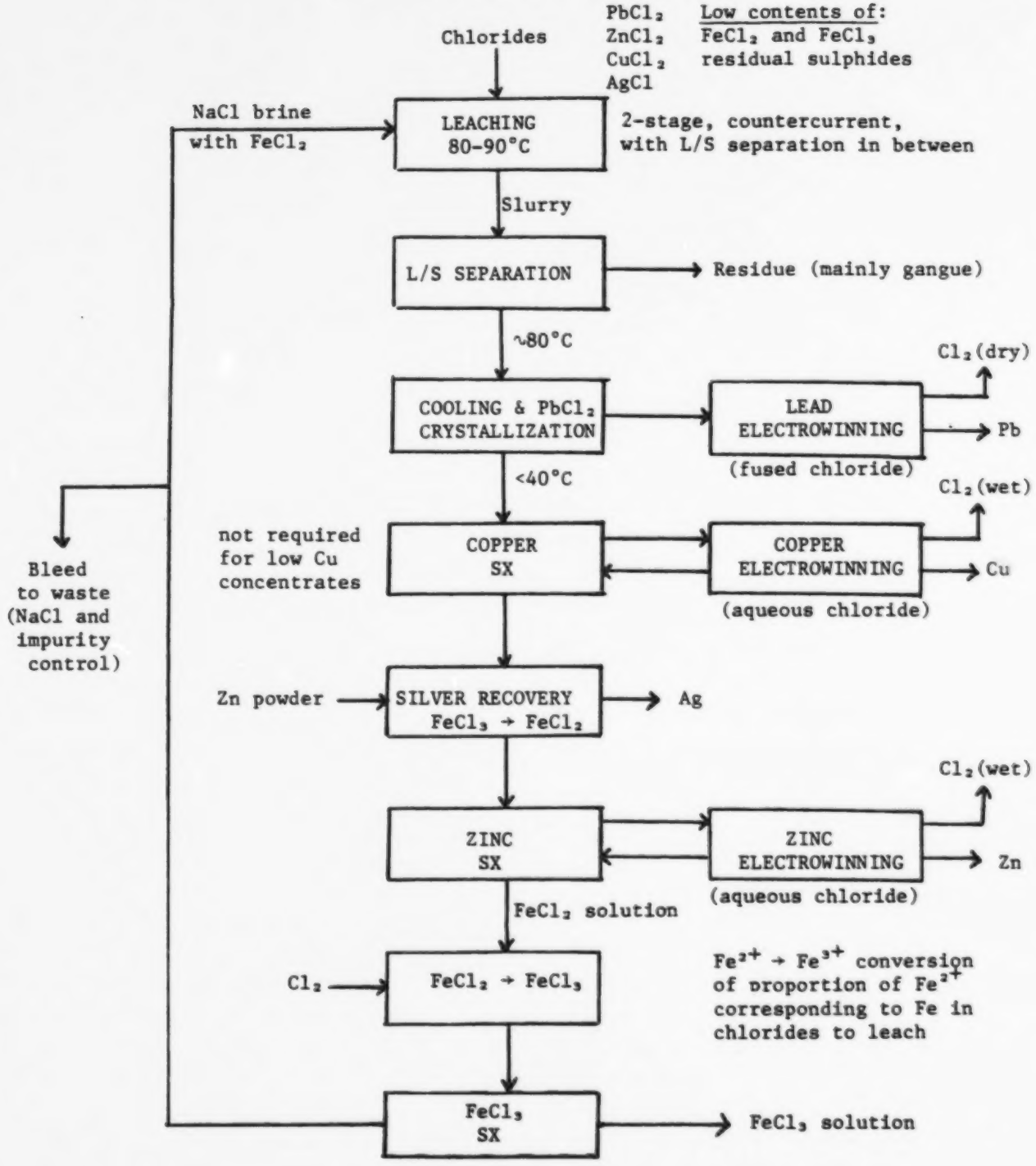
DECHLORINATION FLOWSHEET

Based on: 1. adaptation of Toho Titanium pilot plant flowsheet
2. some $ZnCl_2$ present in deferrinator gas

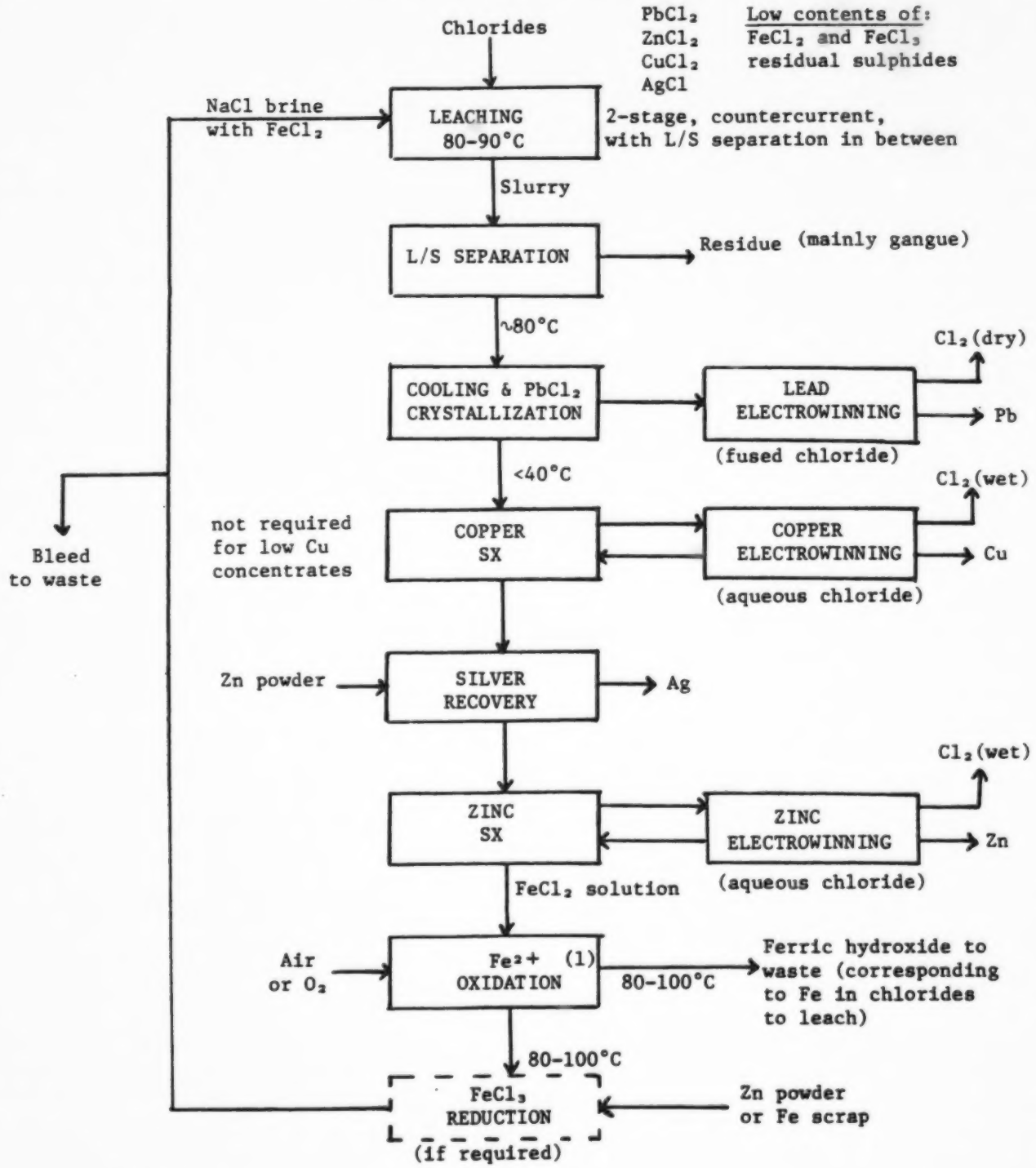

Deferrinator gas
@ ~525°C
~450°C
SOLID $ZnCl_2$ CONDENSER
Impure solid $ZnCl_2$ recycled to chloride melt. Deferrinator melt splash may also have to be removed. Would contain $FeCl_3$.
High temperature condenser may be required to avoid melt splash and $ZnCl_2$ getting into $FeCl_3$
150-170°C
SOLID $FeCl_3$ CONDENSER
Gas (N_2 + excess Cl_2) to Cl_2 recovery
Low temperature condenser as used by Toho Titanium
$FeCl_3$ powder
Fe_2O_3 + $FeCl_3$ dust
Oxygen
FLUID BED DECHLORINATOR ~700°C
Cl_2 gas
COOLER
Fe_2O_3 with <0.1% Cl
Cl_2 gas with excess O_2 to Cl_2 recovery

HIGH TEMPERATURE CHLORINATION PROCESS

Flowsheet 4: Hydrometallurgical Circuit
Iron Control by SX removal as $FeCl_3$



HIGH TEMPERATURE CHLORINATION PROCESS
Flowsheet 5: Hydrometallurgical Circuit
Iron Control by Air Oxidation



REACTION

(1) Fe^{2+} oxidation: $6\ FeCl_2 + 1.5\ O_2 \rightarrow Fe_2O_3 + 4\ FeCl_3$

FIG 3 VAPOUR PRESSURE OF SPECIES OVER MELT

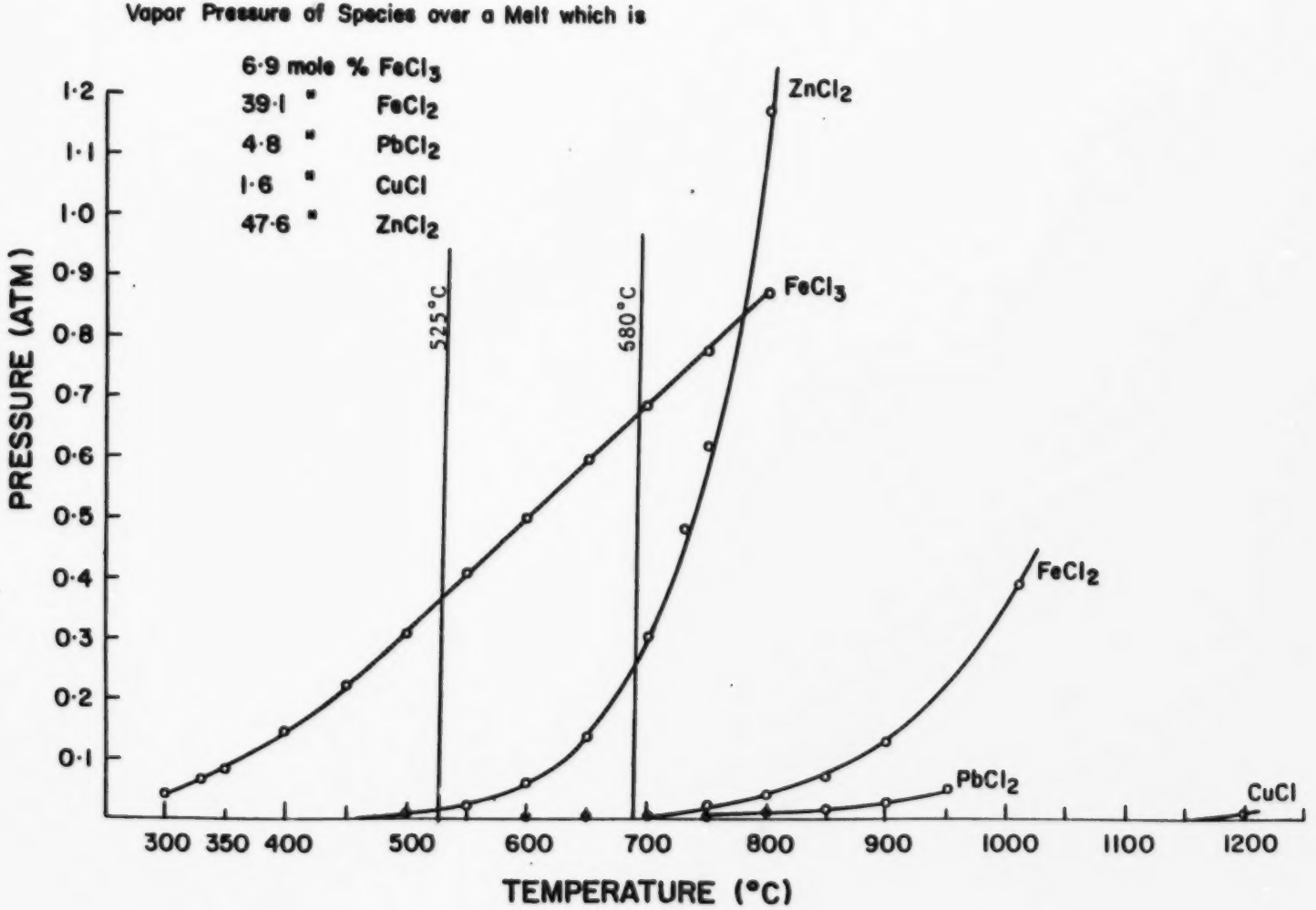
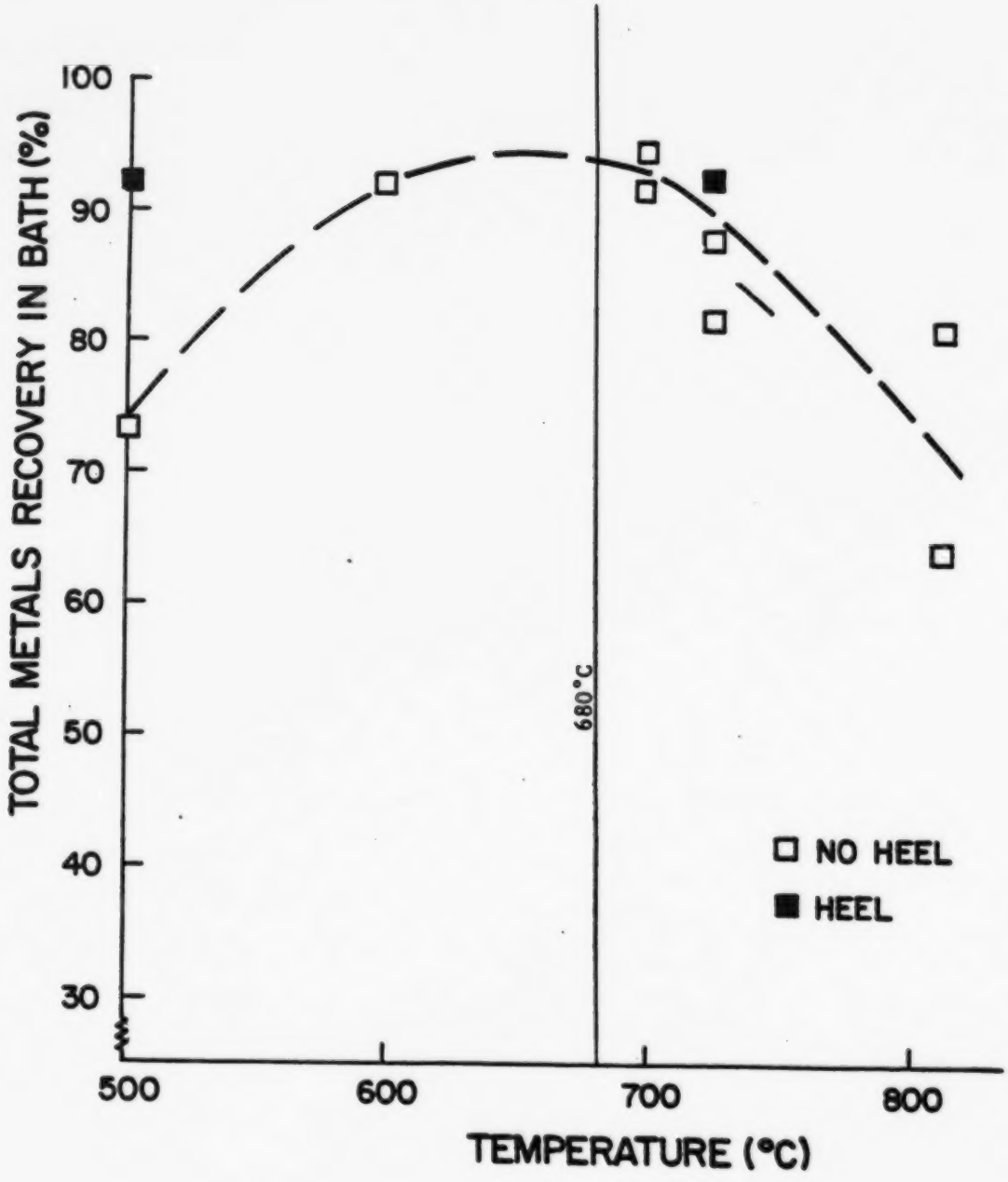


FIG 9 TOTAL METALS RECOVERY AS A FUNCTION OF TEMPERATURE



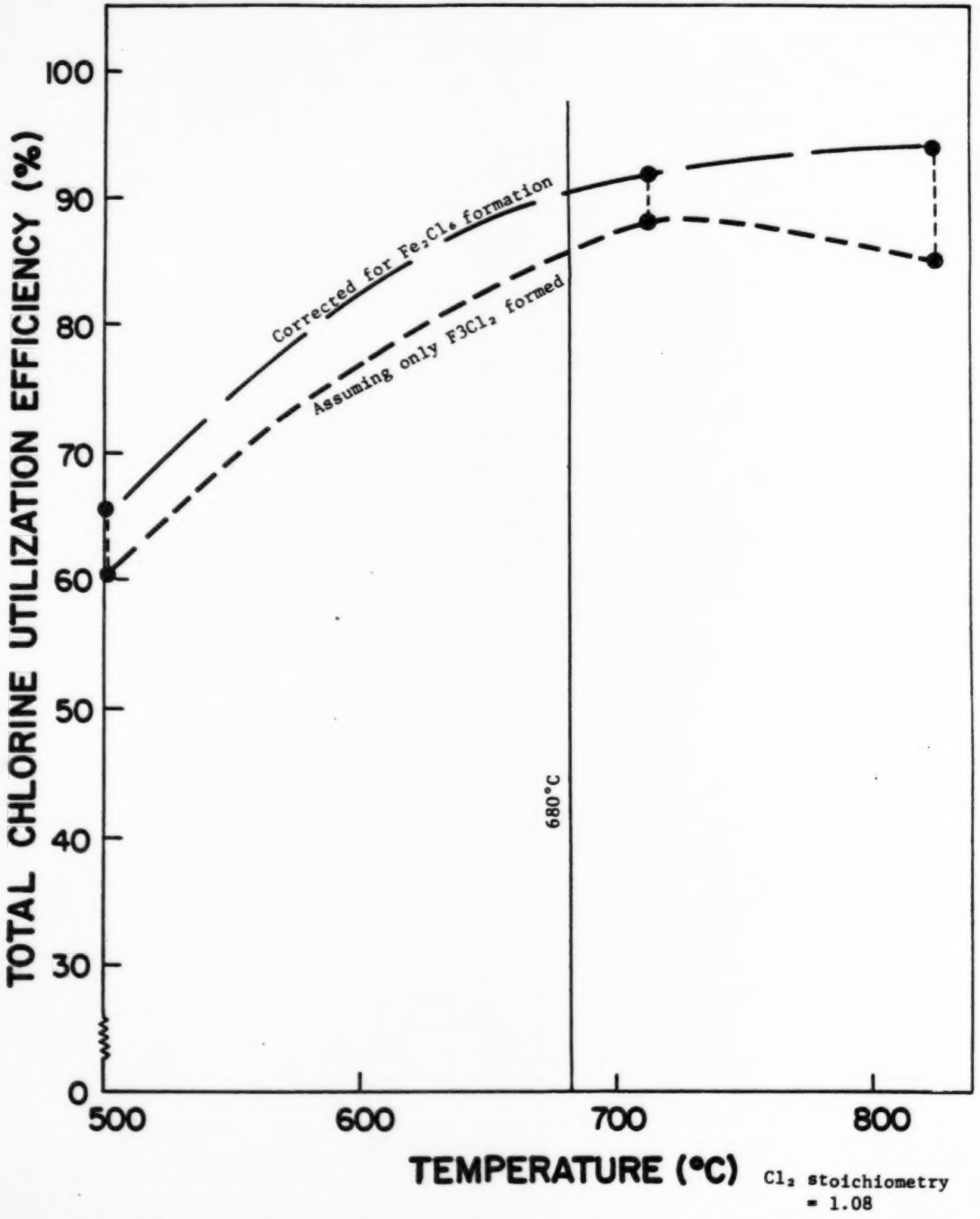


FIG 10 CHLORINE UTILIZATION EFFICIENCY AS A FUNCTION OF TEMPERATURE

FIG 12 EFFECT OF CHLORINATION TEMPERATURE ON $FeCl_3$ FORMATION

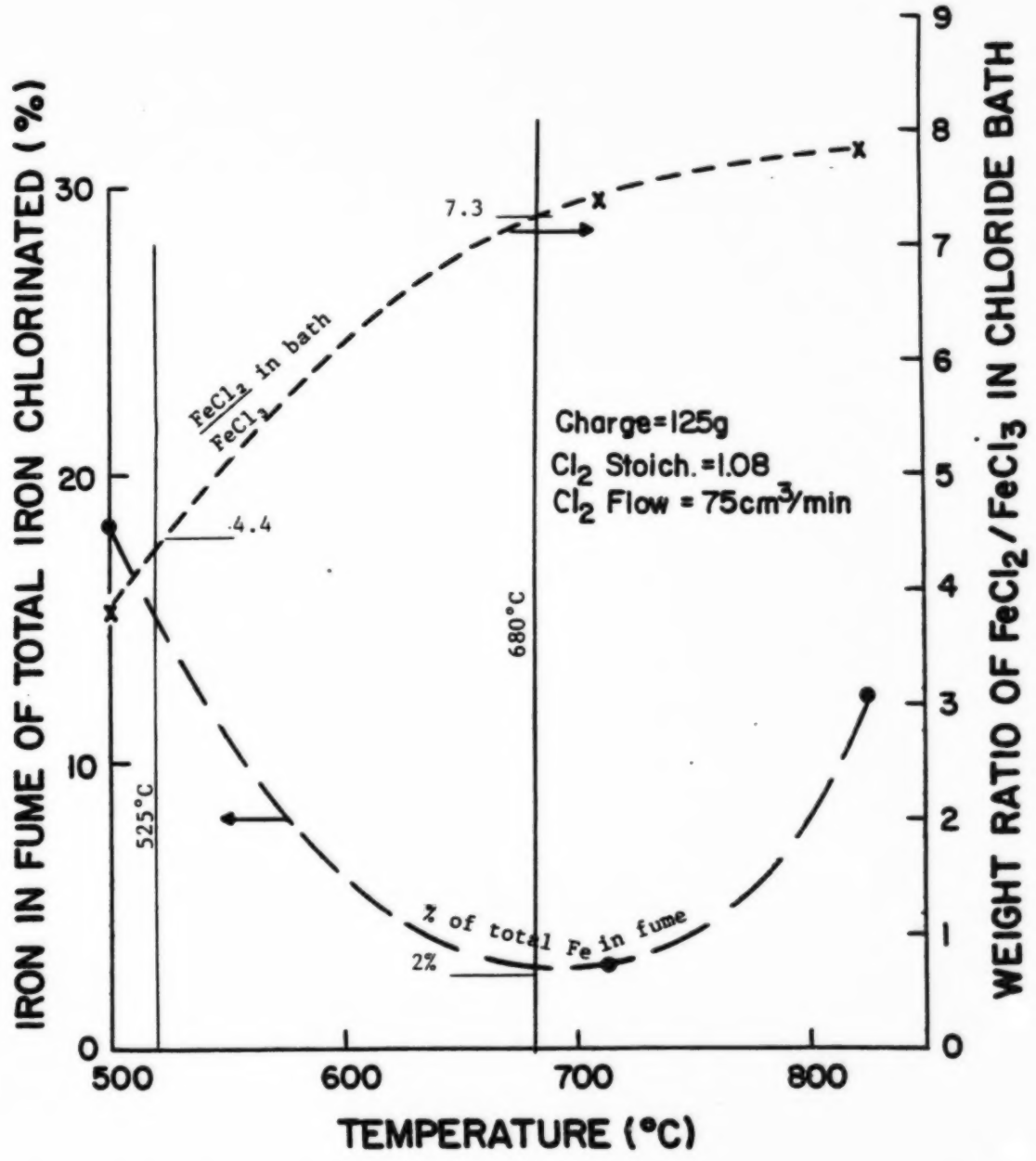
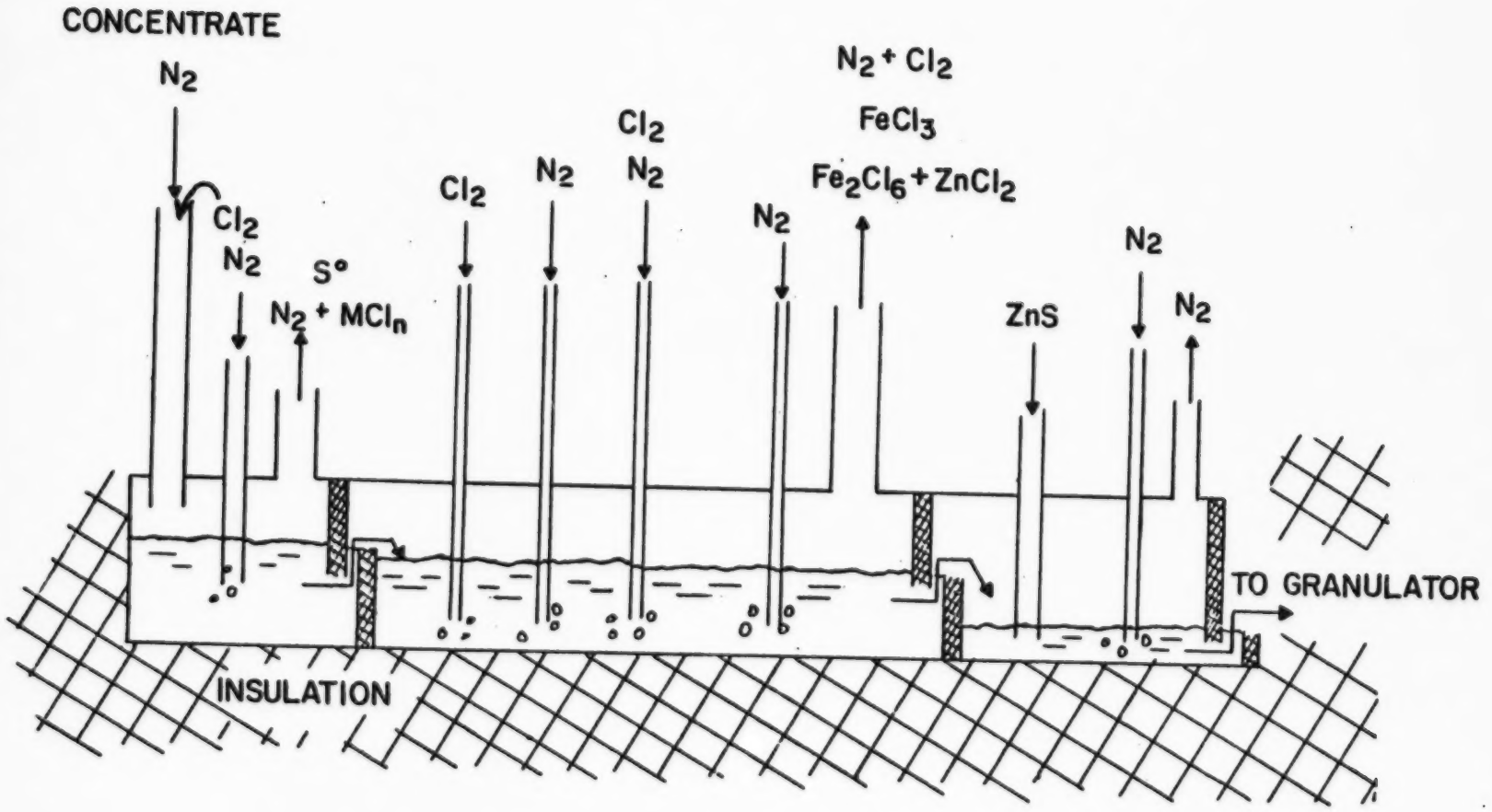
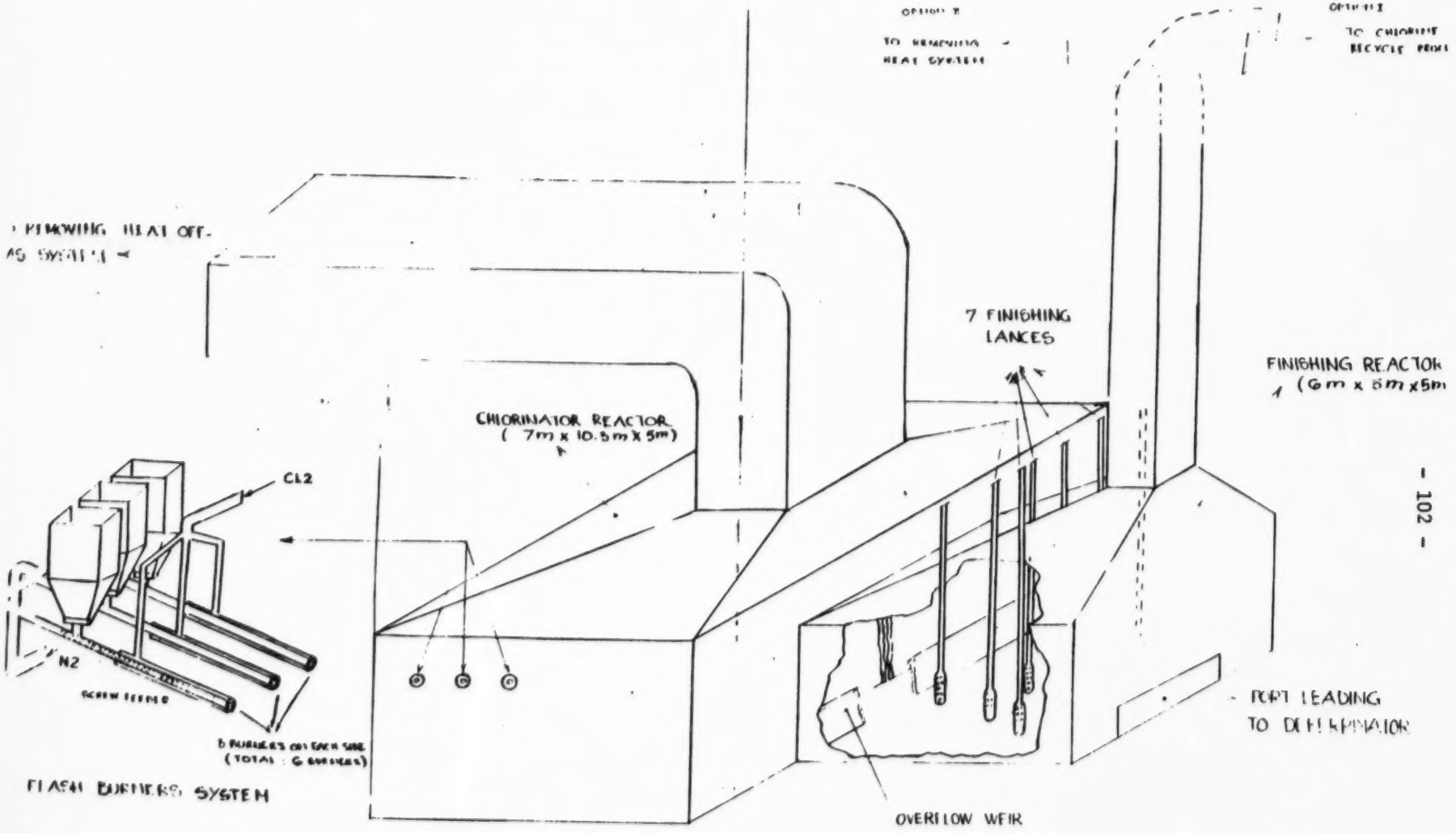


FIG 17 CONCEPTUAL DESIGN OF REACTOR



HIGH TEMPERATURE CHLORINATION PROCESS

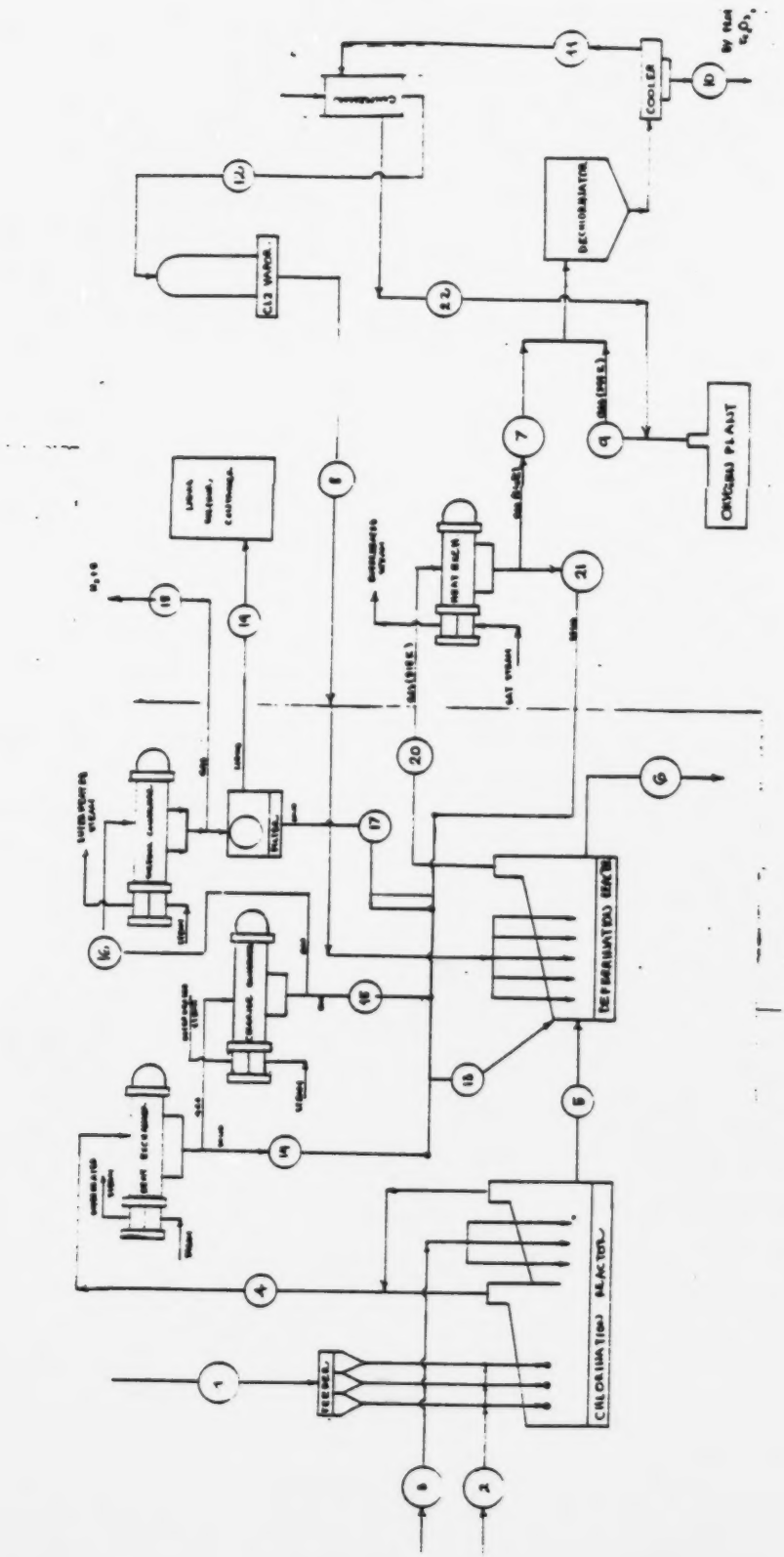
CANMET TROUGH REACTOR CONCEPT



HIGH TEMPERATURE CHLORINATION PROCESS

CANMET TENTATIVE CHLORINATION REACTOR DESIGN

SCALE 1m



HIGH TEMPERATURE CHLORINATION PROCESS

CANMET TENTATIVE MECHANICAL FLOWSHEET

APPLICATION OF DRY CHLORINATION PROCESSES TO NICKEL-COPPER SULPHIDE ORES

CONCLUSIONS

Canadian nickel-copper sulphide ore concentrates would probably respond well to chlorination with chlorine gas at high temperature (say 500°C) and with sulphur chloride at low temperature (100°C or less), insofar as nickel, copper and probably also cobalt would be converted to soluble chlorides.

To achieve economic mill recovery from these ores, however, it is usually necessary to leave in the nickel concentrates an amount of iron, in the form of Fe in the pentlandite lattice, and as nickeliferous pyrrhotite, greatly exceeding their nickel content. This particularly applies to Sudbury ores where pentlandite and pyrrhotite are intimately associated, and where the pentlandite contains significant iron while the pyrrhotite contains significant nickel. Iron present in the concentrate is likely to be extensively chlorinated and solubilized in subsequent leaching.

Removal of large amounts of iron from a leach solution, whether as ferric chloride or hydroxide, would probably be very costly and could cause disposal problems as serious as the SO_2 emission problem chlorination is supposed to solve. The same viewpoint applies to iron removal by $FeCl_3$ volatilization and conversion to Fe_2O_3 in the high temperature chlorination alternatives. In conventional smelting, the iron is disposed of as inert slag.

Removal of minor amounts of iron and copper in nickel chloride solution is known technology in connection with nickel matte refining. Those removal methods, such as removal of iron as ferric hydroxide or as ferric chloride solution by solvent extraction, and copper precipitation as sulphide, for example, would be very costly and maybe would require such a complex flowsheet as not to be practical, if applied to leach solutions with more iron than nickel and copper levels of the same order as nickel. Under practical plant conditions, the removal of large amounts of iron from a nickel solution is likely to entail significant nickel losses.

Cobalt can be effectively separated from a purified nickel solution. Consequently, cobalt recovery should present no problem if the iron and copper

removal problems are solved.

The behaviour of precious metals, in particular platinum metals, in chlorination is difficult to predict. They could split in several streams, rendering efficient recovery difficult.

Because large quantities of iron must be carried through the process, chlorination of Sudbury nickel-copper concentrates would entail handling of large tonnages of molten chlorides and recirculation of a huge tonnage of chlorine gas, assuming that chlorine in iron chlorides is recoverable by deferrination and subsequent dechlorination of volatilized ferric chloride. Capital and maintenance costs of the necessary equipment are likely to be much higher than for conventional smelting and refining.

The outlook for developing a practical, reasonably economic and environmentally acceptable chlorination process does not seem sufficiently attractive to justify spending the sustained research effort and large amount of money which would undoubtedly be required to properly investigate this approach.

EXPECTED BEHAVIOUR OF NICKEL-COPPER SULPHIDE ORES

Nickel and Copper

In the absence of adequately reported experimental evidence it is not possible to draw definite conclusions regarding the applicability of chlorination on nickel-copper sulphide ores, at the three temperature levels applied to complex zinc-lead-copper concentrates.

In Canadian nickel-copper ores the nickel is mainly present as pentlandite which is normally a reactive mineral and which we therefore would expect to respond well to chlorination. Unfortunately, the same applies to iron in the form of pyrrhotite, a mineral prevalent in Canadian nickel ores and difficult to completely separate from pentlandite. Also, iron is present in pentlandite and nickel in pyrrhotite, and the two minerals are closely associated in the Sudbury ores. Consequently, a large amount of iron is likely to be chlorinated with the nickel. Test work on other concentrates containing copper have already

shown that chalcopyrite is chlorinated.

Thus, we believe that Canadian nickel-copper sulphide concentrates would probably respond well to chlorination, possibly within a wide range of temperatures and other process conditions. These concentrates are likely to react with chlorine gas at high temperature and there is some indication that sulphur chloride (S_2Cl_2) will chlorinate nickel concentrates even at quite low temperatures, i.e. at 100°C or less.

Iron

While nickel concentrate chlorination may be metallurgically feasible, we do not believe it to be an economically viable alternative to smelting for the purpose of avoiding SO_2 emissions. To achieve economic mill recoveries, it is usually necessary to produce nickel flotation concentrates which contain more iron than nickel, as already explained. It would therefore be necessary to eliminate large tonnages of iron, either as volatilized ferric chloride in the high temperature chlorination variant, or from a Ni-Cu-Fe chloride solution in the low temperature variant. Iron removal would be very expensive in both cases and is likely to result in environmental problems which could be as serious as the present SO_2 emissions, in view of the large amounts of iron involved. In this connection one should remember that a large proportion of the SO_2 emissions from nickel smelting is also due to the great amount of iron sulphides left in nickel concentrates, in particular those produced from Sudbury ores. In other words, this characteristic of nickel sulphide ores which leads to high SO_2 emissions in smelting, is the same which is likely to cause serious environmental problems in chlorination.

Cobalt

Cobalt is likely to chlorinate together with nickel but this is not a problem since the two metals are relatively easy to separate from a purified nickel-cobalt chloride solution.

Precious Metals

Precious metals, particularly platinum group metals, are economically important in nickel sulphide ores, especially those from the Sudbury district.

Gold and platinum metals form soluble chlorides, including a complicated array of complex chlorides. Most precious metal chlorides decompose at relatively low temperatures:

$$AuCl_3 \xrightarrow{170°C} AuCl \xrightarrow{290°C} Au$$
$$PtCl_4 \xrightarrow{370°C} PtCl_2 \xrightarrow{500°C} Pt$$
$$PdCl_2 \xrightarrow{581°C} Pd$$

Consequently, in the high temperature chlorination process these precious metals are likely to remain, at least in part, in the solid residue from which some of them might be recovered by cyanidation although we consider this very doubtful in practice. If chlorinated by S_2Cl_2, these precious metals might be solubilized in the low temperature chlorination process and then recovered from the nickel leach solution by selective cementation; again, this is highly speculative. The behaviour of precious metals is difficult to predict and might be quite complicated, being partially volatilized or solubilized and therefore split into several streams, which could render difficult their economic recovery. In existing nickel smelting and refining processes, precious metals are gradually concentrated first in matte and then in leach or anode residues sufficiently concentrated for economic treatment in a precious metals refinery.

EXPERIMENTAL BASIS

A 1982 paper[25] describes laboratory scale chlorination on nickel sulphide and arsenide minerals. In the case of millerite (NiS), the only nickel sulphide mineral tested, formation of $NiCl_2$ occurred in the temperature range 440-820°C but was never complete below 820°C. Nickel was however completely chlorinated when a 1:1 millerite-pyrite mixture was chlorinated below 500°C, probably due to the effect on nickel sulphide of $FeCl_3$ formed by chlorination of the pyrite. This is interesting as it indicates the probability that nickel concentrates containing pentlandite and pyrrhotite would react similarly and that their nickel content is likely to be almost quantitatively converted to soluble nickel chloride. Extensive conversion of pyrrhotite iron to iron chlorides must however be expected to occur at the same time, as pyrrhotite is

generally more reactive than pyrite. Copper would presumably be chlorinated to an extent similar to that achieved on complex Zn-Pb-Cu concentrates tested by CANMET under similar conditions.

A U.S. patent[26] assigned to Continental Oil Company describes in Example 2 a small scale test in which pentlandite ore of composition $(Ni,Fe)_9S_8$ was reacted with sulphur monochloride (S_2Cl_2) at below 80°C. After 45 minutes the reaction product was extracted with a NH_4OH solution at pH 11.5. Substantially all the nickel was solubilized as a nickel-ammine complex. Example 1 describes a similar test on chalcopyrite at 100°C for one hour, in which 93% of the copper was solubilized by leaching with a $NH_4OH + NH_4Cl$ solution as a soluble copper-ammonium salt from which copper was recovered by electrowinning with a graphite anode. These laboratory tests indicate that a nickel-copper sulphide concentrate is likely to be effectively chlorinated by S_2Cl_2 at below 100°C and that both nickel and copper can be converted to soluble chlorides at high yields. Leaching the reaction product with an ammoniacal solution leaves the iron as insoluble hydroxide but this liquid/solids separation is a difficult one on commercial scale due to the slimy nature of the hydroxide. Even goethite FeOOH obtained above 90°C has poor filtering and washing characteristics. Hematite is easily filtered and washed but is only formed at high temperature and therefore requires an expensive autoclave operation. The possibility of removing iron as a ferric chloride solution by solvent extraction, is discussed elsewhere in this report. In any case, iron removal and disposal is likely to remain a major technical and economic problem in applying low temperature chlorination to iron rich nickel-copper sulphide concentrates.

Laboratory chlorination tests have been carried out on lateritic nickel ore (garnierite) and charcoal added as reduction agent, with chlorine gas diluted with nitrogen.[27] After 30 minutes at 950°C and a partial Cl_2 pressure of 61 torr, 92% of the nickel was volatilized and recovered as $NiCl_2$. However, 92% of the iron and 33% of the magnesium were also chlorinated and volatilized. These tests were carried out at a much higher temperature than the range considered by CANMET but are nevertheless mentioned because they show that nickel and iron are chlorinated to similar extents, at least at a temperature where the chlorides of both metals are volatilized.

CHLORINATION OF NICKEL SULPHIDES

SOURCES OF INFORMATION

25. S.A. Mikhail, C.R.K. Maclean: "Chlorination of Nickel Minerals", CANMET Report ERP/MSL 82-85(TR); Ottawa, August 1982.

26. A.G. Fonseca: "Recovery of Metals from Sulphur Bearing Ores", U.S. Patent 3,979,265, Sept. 7, 1976 (see example on nickel ore in patent).

27. F.E. Pawlek et al: "Chlorination of Garnierite", paper presented at the 1971 AIME Annual Meeting.